

STATE OF OHIO
John J. Gilligan, Governor
DEPARTMENT OF NATURAL RESOURCES
William B. Nye, Director
DIVISION OF GEOLOGICAL SURVEY
Horace R. Collins, Chief

MISCELLANEOUS REPORT NO. 1

**TENTH FORUM ON GEOLOGY
OF
INDUSTRIAL MINERALS
PROCEEDINGS**

1

RECLAMATION OF PITS AND QUARRIES

2

CARBONATE ROCKS IN ENVIRONMENTAL CONTROL

Columbus
1974



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FOREWORD

This volume contains the papers that were presented at the Tenth Forum on Geology of Industrial Minerals, held at Columbus, Ohio, on April 17-19, 1974. The Forum was sponsored jointly by Ohio State University's Department of Geology and Mineralogy and the Ohio Division of Geological Survey. About 140 geologists, mostly from industry, state surveys, and federal agencies, attended.

The papers are printed in the order in which they were given. First are five reports on various aspects of conservation, reclamation, and land use. Following these are four papers on the use of carbonate materials in controlling acid mine drainage and in fertilizing minesoils. The final six papers are on use of various applications of lime and limestone to control SO_2 emissions from power-plant stack gases. We here record our thanks to the speakers for giving excellent talks and for being prompt in furnishing copy for the present volume. Numerous compliments were received on the high caliber of the technical program.

Following the formal sessions, a half-day field trip enabled Forum participants to view several examples of sequential land use in the Columbus area. One such example was a luxury housing project developed around a lake in a former limestone quarry. We express the appreciation of the whole group to American Aggregates Corporation for hospitality at a recently opened limestone quarry and plant and for providing lunch at their recreation building.

We also acknowledge with pleasure the help of R. J. Anderson, R. S. Bowman, and C. E. Corbató, who, together with the undersigned, made up the local committee.

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CONSERVATION AND RECLAMATION IN THE SAND AND GRAVEL INDUSTRY

by

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ABSTRACT

The sand and gravel industry provides an enormous quantity of materials vital to the maintenance of low-cost construction. There has been little effort to conserve this valuable natural resource. In fact, existing regulations which affect sand and gravel operations act more to waste these materials than to conserve them. Another factor affecting the industry is new legislation requiring the reclamation of worked-out pits. Although such legislation creates many administrative headaches for a sand and gravel operator, there exists the possibility through such legislation of gaining some conservation measures that could be helpful to the industry.

INTRODUCTION

When the program committee suggested that I might make a presentation on a subject which would fall within the purview of the general category of conservation and reclamation in the sand and gravel industry, it seemed to me that a paper on the category as a whole might serve a useful purpose.

First permit me to set forth some information which should serve to establish some parameters by which the nature of the sand and gravel industry can be better understood.

The sand and gravel industry is primarily a supplier of construction aggregates to the construction industry. Statistics taken from the U. S. Bureau of Mines Minerals Yearbook for 1969 (1971) show that during the decade of the sixties over 96 percent of the sand and gravel produced in this country was consumed by the construction industry and that almost 61 percent of the total consumption of construction aggregates by the construction industry was supplied from sand and gravel production.

The latest national statistics published, those for the calendar year 1971 (U. S. Bureau of Mines, 1973) show the total U. S. production of sand and gravel as 919,000,000 tons. The industry, in the not too distant future, should top

one billion tons per year. On the basis of tons produced per year, the sand and gravel industry is the largest mining industry in the United States.

This particular title is being challenged by the crushed stone industry, which contributes the other 39 percent of the construction aggregates consumed, but which is able to market 27 percent of its production outside the construction market.

The national annual per capita consumption of construction aggregates grew from 6.25 to 7.61 tons per person, or over 20 percent, in the sixties. Similar figures for the individual states show a mixed pattern. Contrary to my original assumption that the industrialized higher populated states would have the largest per capita consumption of construction aggregates, Nevada, the state with the smallest population, led all other states. However, in terms of total demand the per capita consumption figures show one important aspect of the construction aggregate industries: the areas of greatest total demand are the highly urbanized areas where the maximum population densities exist.

Historically the sand and gravel industry has been a highly fragmented industry. Today there are several industry giants who individually account for less than 4 percent of the total volume

produced. The 1971 Minerals Yearbook shows production reported from more than 5,500 operations.

An economic analysis of the industry shows that it is a high-capital-cost industry. The ratio of plant investment cost to dollars of annual sales is high. In American Aggregates Corporation this ratio is 2.1/1.0, which is to say that it requires a plant investment of \$2.10 to generate \$1.00 of annual sales. Because American Aggregates Corporation has been a corporate identity since the turn of the century and therefore has had the advantage of acquiring some of its assets prior to a substantial portion of the continuing inflation, the investment-to-sales ratio which we enjoy is less than that which would be experienced by any operation initiated today.

The profitability of any business venture is most accurately measured by the rate of annual return on the owners' investment. This relationship, in accounting terminology, is called return on equity. The historical average return experienced by all U. S. industry has been about 12 percent. The high-capital-cost segment of industry has a historical return on equity of about 10 percent. The smaller return on equity experienced by the high-capital-cost industries may be justifiable on the basis of its steady growth in demand, which in turn suggests a lower risk factor associated with these industries.

Although steady, the rate of growth of demand for sand and gravel cannot be viewed as spectacular. Through the sixties, sand and gravel production figures show an annual average growth rate of 2.7 percent with a variation of 3.3 percent on the average. Such a growth rate fails to arouse much interest in the stock market, and most high-capital-cost-industry stocks have sold for low multiples.

The growth rate experienced during the sixties would cause the total demand to double in about 35 years. When you consider the fact that the first sand and gravel processing plant in this country was built at the turn of the century, just 74 years ago, it is evident that the industry is confronted with the task of duplicating its present capability in less than one-half of the time that was required to achieve its present stature. Should there exist no other problems than those of completing such an ambitious building program, this would still be a rather formidable task.

One other factor (and maybe the most important one) which must be recognized to better understand the nature of this industry is the sensitivity of its product to transportation costs. The cost to the ultimate consumer is a combina-

tion of the plant price for the material and the transportation cost to the point of use. Transportation cost, prior to the recent increases in fuel costs, could be estimated at approximately 5 cents per ton-mile. The 1971 Minerals Yearbook reports the average value of the sand and gravel consumed by the construction industry to be \$1.17 per ton. Therefore, hauling sand and gravel 25 miles will double its cost to the ultimate consumer. For this reason the market area served by any operation is generally within a 20-mile radius. It should be noted, however, that the ultimate benefactor of this limited marketing area is the consumer.

CONSERVATION IN THE SAND AND GRAVEL INDUSTRY

The total resources of any nation determine what relative position that nation may achieve on the scale of worldwide economic prosperity. How well those resources are managed determines how long that nation will be capable of maintaining its relative position.

The people of the United States of America enjoy the highest standard of living of any nation on the planet Earth. This fact attests to this country's abundance of all sorts of resources. But for years we have been acting as if our natural resources, which are vital elements of our total resources, were limitless or as if we could rely upon other nations to provide an assured supply of resources which we had exhausted.

As in the case of most other ill-conceived courses of action, there must first exist a crisis before efforts are initiated to develop a better approach. The existing energy crunch has made it clear that there no longer exists an inexhaustible supply of fossil fuels in this country and, furthermore, that it could be fatal to depend upon the energy-producing resources of any other nation to overcome our deficiency.

Although the present situation can be related primarily to a shortfall in the supply of petroleum, one dare not fail to recognize the total interdependence of the various resources from which usable energy may be derived. Because the people of this nation became obsessed with the idea of cleaning up our air, air pollution laws were enacted; the regulatory limitations of these laws forced many power plants to turn to middle distillates as their source of energy. As the demand for coal dropped, some of the less efficient operators were forced out of business. So the total capacity of the coal industry was reduced from its former level. For the coal-producing indus-

try to be able to assume a greater share of our energy requirement than it previously enjoyed and thereby relieve some of the pressure on our petroleum supplies will require many years and some substantial changes in the environmental laws with respect to some of the oppressive requirements (e.g., highwall and SO₂ limitations) enacted during the height of the environmental movement.

The current shortages which exist with respect to other primary resources such as steel and copper are further examples of the fact that our resources are not inexhaustible.

Sand and gravel also constitute a valuable natural resource of this country. Where are we to find a replacement for the 919,000,000 tons of sand and gravel that were consumed in 1971, should this resource be exhausted? This question assumes greater significance when you add—at a cost less than one-tenth of a cent per pound.

Although the total sand and gravel resources of this country are still quite substantial, we must not overlook the fact that it is the location of these resources that determines how economically the demand can be met. The areas of sizable demand are where the population centers exist. In such areas there are many competing uses for land which has transportation advantage to the center of the marketplace. Those areas which contain sand and gravel are also considered ideal construction sites by land developers.

Webster defines conservation as protection from waste. The only agencies in existence which have had the power to institute conservation practices affecting our nation's sand and gravel resources are the local zoning boards, which exist in most of this country's more populated areas.

Unfortunately these agencies have done much more to waste this resource than to conserve it. One of the first prerequisites for developing a zoning plan for any area is to develop a land-use map. The land-use map should designate specific areas for every type of activity that will be necessary to maintain the economy of the area in question. Most land-use maps do not provide any specific areas for sand and gravel excavation. The extraction of sand and gravel is generally considered as a special use which may be conducted in an industrially zoned district through the granting of a special permit by the zoning board of appeals.

The first trick is to find a sand and gravel deposit in an industrially zoned tract. Since industrial districts are generally located outside of the drainage valleys in order to avoid the risk of flooding, the odds are that there are

no sand and gravel deposits located on industrially zoned tracts. Therefore a prospective operator must first obtain a change in zoning from some other district to an industrial district—a request which has a very low probability of success. Second, he must secure a special-use permit. A public hearing must be held on each request. If the first requirement doesn't get you, the second one most certainly will.

If the operator overcomes these two obstacles, he is then confronted with another problem. Zoning ordinances, like legislative bills, are drafted by people who simply draw from the text of existing instruments' language provisions which seem to accomplish what they feel would be desirable in the area for which they are concerned. Over the years I have observed the setback limitations, which determine how close a sand and gravel operation may be conducted to the property line, extended from 50 feet to a fairly common 300 feet and in some cases to 500 feet. When I asked the framers of such regulations how they arrived at the particular number in their resolution, they usually responded that it was the biggest number that they had found in other resolutions. These people did not realize that a 300-foot setback requirement on a 100-acre parcel would result in but 52 acres upon which excavation could be conducted. This situation constitutes a horrible waste of our sand and gravel resources. But that fact does not change the setback limitations in many zoning resolutions.

Because most of the people involved in the legislative and the judicial functions of local zoning are overly responsive to the pressures of their neighbors and are not qualified to determine what constitutes reasonable operating limitations upon the sand and gravel industry, the existing zoning structure can never be looked upon as a means of conserving our sand and gravel resources. Consequently there is no public effort, other than that of the industry itself, to promote the conservation of our sand and gravel resources.

RECLAMATION IN THE SAND AND GRAVEL INDUSTRY

Since the 1920's American Aggregates Corporation has been recognized as the leader in the sand and gravel industry in the reclamation of worked-out pits. Although originally this effort was initiated because the founder of our company felt that our industry could not expect to survive if the aftermath of its operations was despoiled land, we quickly discovered that there existed a substantial demand for properties that

were effectively reclaimed. I would like to point out that to me it is quite exciting to be a part of an industry which can make a reasonable return on its primary business of producing sand and gravel and, at the same time, create landforms that could never have existed had the primary part of our business not taken place.

Several years ago when the environmental fever, which has so engulfed our national priorities, was at its peak, the federal government initiated legislative hearings upon the subject of an all-industry surface-mining reclamation bill. The National Sand and Gravel Association appeared before the legislative committees of both the House and Senate to offer testimony in support of industry's contention that there was no need for the sand and gravel industry to be included within the purview of the bill. One reason for this assertion was that most of the industry was already required to reclaim through either local zoning or state reclamation laws.

The gist of the balance of the testimony can be derived from the 919,000,000 tons of production reported for 1971. If we assume that the average deposit had a 40-foot working face and that 85 percent of the material excavated was sold (assumptions which I feel are realistic) 10,700 acres would have been excavated to yield the tonnage for that year. Because there are over 5,500 sources from which that production was reported, the average acreage affected per operation would be less than two acres a year.

Now I must admit that averages can be misleading. In order to give you some idea of the range of acreage which may be affected by a sand and gravel operation, the sand and gravel operation in south Columbus is one of the plants listed in the top 10 nationwide on the basis of annual production. The sand and gravel operation at this plant affects approximately 20 acres per year.

Therefore it was industry's further contention before the legislative committees that the acreage affected by each sand and gravel operation was so small and that there were so many operations that the cost of administering the program would exceed the benefits to be derived therefrom.

The federal committees apparently heeded the testimony of the noncoal surface miners, for the federal bill in its present form covers coal strip mining only. But the bill mandates further studies to determine whether federal legislation should be enacted to require reclamation by other surface-mining industries.

Like most of the federal acts affecting our environment, the Surface Mining Reclamation Bill contains a provision which provides for state implementation if the state's requirements are at

least as stringent as those set forth in the federal act. Many of the states, in anticipation of the federal bill, initiated legislative action such that they could assume the regulatory function at the state level. Ohio is one of those states.

I have had the opportunity to work with a subcommittee of the Ohio Senate Committee on Agriculture, Conservation and Environment, which for over 12 months labored with representatives of the Ohio Department of Natural Resources and representatives of the affected industries in an effort to prepare a bill which would be compatible with each group.

The result of this joint effort, the Surface Mining Reclamation Bill (SB 165), was passed by the Senate during the last week in March (1974). The bill must now be considered by the House.

The primary purpose of SB 165 is to assure reclamation of those areas affected by sand and gravel, limestone, clay, and shale mining. The bill also includes a number of regulatory provisions which affect how the operations of these industries can be conducted.

I personally am not satisfied with the present form of this bill, but must confess that I do not have a solution for my primary objections.

Webster defines reclamation as restoration to a useful state. This definition is the key phrase within the reclamation provisions of SB 165. However, what constitutes adequate reclamation in any situation is a function of what use is planned for the property after the mining operations have ceased. After-uses could range from a sanitary landfill to a lakeside residential development. Obviously, different reclamation standards should be required not only for these two extremes but also for the myriad of potential uses that lie in between. Because it would be impractical, if not impossible, to set forth in the law itself reclamation standards for all of the possible end uses, the only alternative is to empower a governmental agency with the authority to specify the standards, based upon the situation in each individual case.

This eventuality could be very dangerous. For this arrangement to function properly, there must be a presumption of expertise on the part of the governmental agency. Such expertise does not now exist, either inside or outside of government. As the Senate subcommittee sought solutions to the problems that the representative of any one of the affected industries felt that his particular industry might face, it was obvious that the operating conditions in each industry were substantially different and that the so-called experts from the other industries could not offer viable solutions for problems outside their own industry.

The general requirements of SB 165 follow the guidelines set forth in the original federal bill. Each operator who wishes to continue in operation after the effective date of the act must apply for a license to operate. (Someone should be training a lot of people in the art of developing reclamation plans which are compatible with the operating procedures followed in each of the affected industries, for "a complete plan for mining and reclamation of the area to be affected" is required with the application.) The Chief of the Division of Reclamation may grant a license if he determines that the proposed reclamation will fulfill the purpose of the act. Such permit shall be for a period of 10 years. There is a requirement for periodic inspections by the Division and annual reports by the operators. Finally, the operator must provide bond to assure that the reclamation will be completed.

It would seem that a bill which appears to be so simple to describe would also be easy for industry to live with. Such a conclusion is purely illusory. It will in fact require a number of years from the effective date of the act before all of the involved parties will recognize the true impact of this legislation.

As I stated earlier, there have been a number of other states which have been working on similar legislation and which have enacted surface-mining reclamation laws. One such state, Colorado, has enacted a unique statute, which is worthy of some discussion.

The Colorado Surface Mining Reclamation Law affects all of the surface-mining industries in the state. The general provisions of the act are similar to those contained in SB 165. However, there is a second section to the Colorado act which states that the natural resources covered by the reclamation law constitute valuable resources of the state in general. Recognizing that such resources are not inexhaustible, the State Geol-

ogist is ordered to make an inventory of same and to advise the local zoning boards of the locations of these deposits. Each local zoning board is then instructed to set these areas aside until the natural resource has been utilized.

This action is an example of the ultimate in conservation. But I suspect that the courts will determine this requirement to be unconstitutional. First, I would like to offer my congratulations to this assembled group, for the author of this act was a professional geologist, who is presently a member of the Colorado Legislature. Second, it is interesting to note that a state which does not have the population density of many other states and, therefore, has less total demand for construction aggregates has recognized the impending danger with respect to the wasting of its natural resources and has attempted to do something about it.

American Aggregates Corporation for over 15 years has been confronted with the problem of securing from local zoning boards the right to mine upon new properties. Despite our record of reclamation upon all the properties which we have affected, we rate our chances of successfully achieving the necessary zoning such that we can operate on a property near an urbanized area at about 50 percent.

This fact in turn suggests that about 50 percent of the sand and gravel resources which exist within the areas in which we operate are being forever denied for public consumption. When you add to this 50-percent loss of available reserves the additional losses occasioned by the unrealistic setback restrictions found in most zoning resolutions, there exists an unconscionable wasting of this natural resource.

There must be a method found to prevent such waste. Hopefully, the state of Colorado has taken a step which may indicate the way to solve this problem.

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Washington, D. C., U. S. Dept. Interior.

INFLUENCE OF GEOLOGY ON PIT AND QUARRY REUSE PLANNING

by

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ABSTRACT

In preplanning the reclamation of a pit or quarry the geology of the site is the name of the game! The planner must know the parameters of the deposit, the quantity and kind of earth materials to be removed, and the amount and nature of the materials to be left behind or wasted as the result of processing the marketable product. With many states and most local jurisdictions requiring reclamation plans prior to the issuance of mining permits, the need for accurate and complete data concerning the geology of the site becomes increasingly important. The producer need only know that marketable materials are available in sufficient quantity to make the mining operation economically feasible—the planner, in order that the land may be reshaped for a useful purpose, must have reasonably precise information as to the dimensions and configurations of the pit or quarry following extraction and the amount and type of materials available on the site (or in some cases offsite as well). Therefore the geology of the site is of major significance in determining the land forms and use capabilities of the property upon completion of the mining process.

Planning reuse requires a good deal of information about the deposit, the operational program, the types of equipment to be used, and the philosophy of the producer. It will also involve consideration of external factors—land use in the vicinity, environmental influences, and public regulatory measures. The planner's experience and study of the physical and cultural characteristics of the site and adjoining area provide him with a basis for formulating a reuse program that is consistent with the characteristics of the deposit and the configuration of the exhausted pit or quarry.

Preplanning reclamation of a pit or quarry requires a determination of the land forms and in places of the water areas which will be, or can be, produced as a result of mining the resource. Consequently the shaping of the land for a new use following mining becomes the fundamental objective of the preplanning program, and the basis for formulating the new land and water

forms is the quantity and quality of earth material available for that purpose in relation to the dimensions and shape of the pit or quarry following the extraction process. It is therefore a matter of critical concern for the planner to be fully informed as to the precise nature of the deposit and all of the parameters related to it—surface, depth, shape, presence or absence of deleterious materials and other sources of waste, pattern and progression of the mining operation, and type of equipment; most of this information can be and should be supplied by the geologist, with the balance coming from the producer.

To illustrate the influence of geology in preplanning the reuse of a sand and gravel pit, I am presenting a case history of a preplanning program, in which I am currently involved, which will serve to illustrate both the preplanning procedure and some of the problems encountered in opening a new operation. Because this case reveals some interesting aspects of the whole sub-

ject of reclamation of pits and quarries, I have chosen to present it because it is not in the Midwest, but in California, where the requirements for a preplanning program for a sand and gravel or quarry operation are much more detailed and stringent than in this section of the country, and because the geologists involved are not likely to be in this audience.

A study was made of the Williams Canyon deposit, located in Orange County, California, just below the Los Angeles area. Orange is the fastest growing county in the United States. It is also a county which is rapidly exhausting the readily available aggregate materials now being extracted from river and stream beds. The producer's ownership is about 840 acres, the identified sand and gravel deposit, some 195 acres. The extraction area lies in a rather remote location; it is $1\frac{1}{2}$ miles to the Santiago Canyon Highway, in a region of ridges and canyons in the Santa Ana Mountains. The area is virtually wild country with only three small residences to the northwest being occupied; Silverado Canyon to the north and Modjeska Canyon to the south are somewhat more intensively used. The Cleveland National Forest lies to the east.

Study of the area by the geologist included an examination of all of the available literature and site inspection, including the excavation of 12 trenches and walking of the area to identify contact surface exposures of the aggregate material where it is bedded on the underlying bedrock. The material is identified here as unconsolidated terrace gravel, underlain and bordered by volcanic and metamorphic formations, with some Recent Quaternary alluvium. The extraction area included only the area of terrace gravel lying within the property controlled by the producer.

This is rough country—the northwest limit of the extraction area has an elevation of about 1,350 feet above mean sea level and the area is 150 feet above the canyon floor to the northwest; the northeast edge of the extraction area is at an elevation of 2,350 feet, 1,000 feet higher than the western edge; the intervening area consists of a series of knobs and ridges composed of the aggregate material.

The depth of the gravel ranges from 0 to 350 feet and the material occurs in a gently sloping and fairly uniform bed. The volume of material here was estimated as being approximately 100 million tons, of which some 3 to 5 percent will have to be wasted as fines.

As geologists, you would probably be interested in further technical aspects of the geologist's report, but that would take much more

time than is allotted to me, and furthermore, what I have related is roughly sufficient to the planner to proceed with the preplanning studies and to prepare the various plans required by the County Planning Commission for the operation and reuse of the land.

The entire deposit area was divided into 10 extraction units ranging from 14 to 30 acres in area and representing a series of benches or terraces rising in elevation from west to east and accommodating the general drainage pattern of the area. The final base grade following extraction is above the lower limit of the marketable material described by the geologist.

The geologist reported that the top 5 to 10 feet of the deposit consisted of "weathered material" containing a higher percentage of fines and some clay that make it less desirable for concrete aggregates than the fresh material below. Another consideration at this point was that of controlling erosion of the freshly opened excavation units and of doing what we could to "hide" from public view, at least in part, the raw material being mined. Consequently we proposed that the weathered material for each of the units be stripped and moved to the lower edges, producing a 15-foot high berm, on the average, adjoining all of the drainageways. This would pond runoff waters until they have an opportunity to percolate into the ground. Although this area receives only 9 to 12 inches of rain a year, the total annual rainfall may occur in only a half dozen storms, creating severe erosion problems. The planting of the berms for screening effect also assists to hold them in place.

Generally, the sequence of the mining operation begins in Area 1 at the west and progresses in order to Area 10, with mining in each area being conducted from the highest elevation to the lowest in 50-foot layers. In some areas there may be only 5 such layers; in others, there would be 6 to 10 layers.

A further requirement of the county is that of an operations plan. The flow of extracted material from the deposit is by means of a belt conveyor to the processing plant and then by truck from the plant to markets in the area. It is proposed that not more than two of the extraction units will be open at any one time and that, as the mining is completed in each unit, the stockpiled material will be spread over the bedrock of that unit to create the finished grade of the terraces.

Which brings us to the question of reuse. The total area of usable lands is about 155 acres or about 80 percent of the 193.8 acres disturbed by mining. The county requires a reuse plan—and yet here is a program that at the very minimum has a life of 20 years and more likely a life of 30

to 40 years. While I am a firm believer in advance planning, any attempt to be definitive in terms of precise use of such lands at a point in time 20 to 40 years hence is, in my opinion, unwise. My approach to this matter is to ascertain the maximum or optimum usability of the lands in question so that they may be adaptable and available for any one of a series of uses when the time for reuse arrives. Consequently, in this instance, we proposed the adaptability of the exhausted site to a series of potential uses for these lands.

1. Some judicious planting and seeding could cause these lands to revert to their natural state, the only change from the present being topographic. Revegetation with native plants and grasses could be readily accomplished.

2. This property would make a great recreation area—good access is available and splendid opportunities exist for camping, picnicking, family cabin use, and golf. Because these lands adjoin the thousands of acres in the Cleveland National Forest, almost unlimited opportunities for outdoor recreation exist. The development could be public or private.

3. The present pressure for residential lands in Orange County today is almost unbelievable! Twenty to 40 years hence it is not likely to be any less. One plan envisions clusters of townhouses or apartments—but there could well be even more intensive use in the form of high-rise structures. The space is available and usable for a fairly high density of residential use.

4. Ranchettes—homes with facilities for keeping horses and ready access to interesting and extended horse trails—are very popular today in this county. Such a plan proposes a very low-density use for that purpose: $\frac{1}{2}$ -acre lots for families utilizing common stables and $1\frac{1}{2}$ - to 3-acre lots with private stables—the lands are perfectly adaptable for such use.

A planting design has been proposed for use following the removal of the sand and gravel and the regrading to the proposed contours. Typical planting situations are for moderate to rolling slopes or for steep slopes and ridge lines. Plants proposed for each type and a list of suitable plant materials to be used are included in the design.

In a review of this proposal in a work session, the County Planning Commission was favorably impressed and referred it to staff for further study. A question was raised by one of the county departments as to the validity of the geologic information, even though the producer retained a consulting engineering geologist of outstanding professional ability from San

Francisco. This man studied the original geologic report and corroborated its findings; however, the Planning Commission requested the producer to reexamine that subject and to resubmit the project.

Subsequently, the producer retained another consulting geologist, who was also very familiar with the geology of the area and who studied the literature and the site and came up with somewhat different conclusions. The first and second consulting geologists then collaborated in the preparation of a new geologic map, sections, and a report and so—it was "back to the drawing board!"

Principally, the new map identifies three major faults in the deposit area and suggests that the terrace gravel identified in the original geology is in fact the Trabuco Formation (Cretaceous)—the reddish matrix facies; interlayered red and gray facies, and gray facies—and that the material extends beyond the original area, increasing the deposit area to 225 acres. However, all three types are suitable aggregate; the total amount of material available increased by some 16 percent, from 101.8 million tons to 117.3 million tons. Also identified are the conglomerate, volcanic, and metamorphic bedrocks.

New sections portraying the major faults show relative displacements, bedding attitudes, trend and inclination of bedding, or crude stratification. This is a totally different condition from that portrayed with earlier information.

An analysis of the new geology reveals that if the total amount of aggregate material (above bedrock) were to be removed from the 225-acre deposit area:

1. The maximum amount of material would be produced, but it
2. Would leave a steep-sided pit with
 - a. Thirty-two acres usable land (less than 35 percent slope) as compared with 155 acres in the previous study,
 - b. Four drainage pockets—the "breaks" at the faults are 50 to more than 250 feet—and
 - c. Usable land inaccessible, and it
3. Provides unsatisfactory solution in terms of the floor of the pit following extraction and would be unacceptable to the county, because of:
 - a. Drainage problems,
 - b. Literally zero residual value of land for any intensive use, and
 - c. Certain disapproval by the Planning Commission.

Additional studies were made to determine how some of the problems identified in the above

analysis could be overcome. The first, Study A, indicated that the maximum amount of material could be produced and a satisfactory base grade for the pit could be achieved through:

1. Grading by means of cut and fill to produce
 - a. One hundred nine acres usable land
 - b. Adequate drainage for the low points, and
 - c. Accessibility from the west and north by means of a draw paralleling proposed zoning boundary, but
2. Such grading will be costly, requiring 5.25 million cubic yards of cut, this material to be utilized to produce the needed fill. Obviously the cost of such cut in hard rock makes this solution impractical.

The second look at the problem, Study B, also:

1. Produces the maximum amount of material,
2. Suggests a more moderate amount, 1.4 million cubic yards, of cut, but will require substantially more yardage (4.4 million cubic yards) of fill brought in from offsite.
3. Such grading provides
 - a. One hundred five acres usable land,
 - b. Drainage for the low areas, and
 - c. Accessibility the same as in Study A. Presumably such grading will be less costly than in Study A (only 25 percent as much cut), and the balance of the fill would have to come from offsite, sanitary landfill, for example.

The third look, Study C:

1. Suggests utilizing only as much of the sand and gravel as will leave the pit bottom contours essentially as proposed in Study B, after grading as proposed in that study,
2. Reduces the amount of sand and gravel extracted by almost 18 percent or about 20 million tons of material,
3. Provides 105 acres usable land,
4. Accommodates drainage, and
5. Allows accessibility to usable lands.

This project is currently on standby; the client is exploring the many alternatives (Studies A, B, C, etc.) open to him before proceeding to complete the plans and again apply for the required zoning change. The extensive impact of geology on the preplanning of the reuse of a pit is evident.

Two consulting geologists, using the same base source materials and conducting their own field studies, have come to two distinct descriptions of the nature of the deposit. The third consultant, an engineering geologist, very highly regarded professionally, joins the two investigating consultants, however, in agreeing that perhaps the original geology, or the new geology, or something in between, may be correct. But when the planner is called upon to preplan a reclamation program that he can defend to a planning agency, he has to know what condition he can expect following the extraction of the sand and gravel. It can be noted that the geology exerts a strong influence and has a profound effect on the preplanning program; all we ask of the geologist is, "What is the pit going to look like, and what materials will we have available for land shaping, after mining the resource?" We'll take it from there.

Because of technical problems it was not possible to reproduce the slides that accompanied this talk.

ASSETS THAT CAN BECOME LIABILITIES

by

M. R. Leonard
The Standard Slag Company
Youngstown, Ohio

ABSTRACT

It is estimated that between 5 and 15 pounds of solid waste are generated monthly by each individual. Finding a final resting spot for such waste is an important matter. In the "good ole days," dumps of every description and condition were available. Not so now. Almost all states have adopted and are enforcing strict regulations regarding the disposition of solid waste. Many companies, owing to the nature of their business, have potentially good waste-disposal sites available. Cleveland Quarries Company falls in this group; but in spite of our having state and county permits, opposition by the local community denied us the opportunity to provide a needed local service.

Those of us that are in the business of supplying natural aggregates to the building industry find ourselves in a dilemma. Obviously, natural aggregates are those removed from the ground and generally processed in some manner. It goes without saying that to excavate creates a hole. Prior to removal of the resource, a tract of land is a valuable mineral asset, but it can quickly enter the liability category when a gaping hole results. What with motorcycles, minibikes, snowmobiles, and the like, worked-out quarries and sand pits are natural magnets. Removal of sandstone over the years has resulted in numerous holes of various sizes and shapes. The desire to remove one of these holes from the liability category prompted our company to conduct an extensive investigation into solid-waste disposal.

Cleveland Quarries Company of South Amherst, Ohio, is a wholly owned subsidiary of The Standard Slag Company and is reputed to be the largest producer and fabricator of sandstone in the world. The company is the outgrowth of several individually owned quarries that started in operation in the mid-1800's. The property consists of 883 acres and stretches from Ohio Route 113 to the Ohio Turnpike. Tops of many of the huge derricks used to lift blocks of stone are visible to passing motorists. Annually hun-

dreds of tourists stop for a look at this unusual operation. Unfortunately at this time we are not able to provide the general public a tour, but some consideration is now being given to public accommodations such as are provided at the granite quarry in Barre, Vermont.

Amherst sandstone (Berea Sandstone, Mississippian age) has a natural beauty of color ranging from deep reds, browns, and yellows to dark and light grays. Commonly lines of stratification or bedding are exposed in section. Where there have been shallow-water deposits, Amherst sandstone offers unusual ripple impressions, rill marks, wave lines, and, in remote cases, traces of various fossil animals.

As a result of over 100 years of quarrying, two large tracts have been depleted. The Buckeye Quarry covers 25 acres and extends to an awesome depth of 240 feet. The larger #6 quarry covers 75 acres and is 160 feet deep. It is estimated that #6 yielded over 500,000,000 cubic feet of quality stone. Considerable exploratory drilling has been done and it has been determined that quarry #6 is surrounded and underlain by shale. As a result of the presence of the impervious shale, it was decreed by various state officials that such a worked-out quarry could and would make an ideal final resting spot for solid waste. In addition, #6 does have a roadway that leads to the bottom and

that would accommodate vehicular traffic.

With this thought in mind, we began our research in the handling and disposal of household, commercial, and industrial waste. We of course know that the day of dumps and open burning has passed. Incinerators, even those only a few years old, do not meet today's emission standards. Technology has produced environmentally approved incinerators, but at a cost of several million dollars each. Our goal was to develop and operate an approved landfill that would accommodate the disposal needs of Lorain County, Ohio, without the necessity of incineration. Paramount in our minds was the use of private land and private capital as a service to the community at a reasonable cost. Little did we realize the problems that lay ahead.

Although the state of Ohio permits the land-filling of unprocessed waste, we felt that the "Cadillac approach" of processing such waste would be most desirable and acceptable. We spent many months investigating the machinery that is being developed to process and handle solid waste. We found several companies "working at the problem," but few who actually had a plant in operation. One company that did have an operating plant was the Heil Company of Milwaukee, Wisconsin.

In 1966 the Heil Company had entered into an agreement with the city of Madison, Wisconsin, to pulverize household refuse under a United States government grant provided by the Solid Waste Disposal Act of 1965. The results were most impressive. The plant produced a "milled" refuse that could be ultimately disposed at a landfill site without the use of daily cover.

The process is quite simple. The regular street packer-trucks dump their loads into a hopper, from which the trash is conveyed by a rubber belt to the top of a vertical mill. The material falls through the mill as rotating hammers shred it into pieces hardly larger than 2 inches square. As the biggest percentage of trash is paper or a paper product, the ultimate residue is much like confetti. Of course trash contains table scraps and other liquid-producing items, but during their trip through the mill such items are so thoroughly disintegrated that it is impossible to find any trace of them in the final product. In fact, it is not possible for rats, birds, or other animals to survive at the landfill, as tests conducted by the University of Wisconsin have proved. As the bits of refuse placed in their final resting spot are small in size, they will not become airborne even in a strong wind.

Believing that we really had found the an-

swer, we organized and sponsored a visit to Madison by some nine Lorain County officials, including the three county commissioners. So that the trip would have adequate news coverage, reporters from two area newspapers also made the trip. Having viewed the operation before the trip, we believed that it would sell itself. The reactions during the tour were precisely what we anticipated. Some of the comments quoted in the newspapers were: "It's amazing—something to look into if we are to meet state requirements"; "I see it as a great advantage over a regular landfill"; "We're looking at this and can see what it is, but how can you make the people in Lorain County believe it?" The last comment anticipated our ultimate failure.

We engaged Jones & Henry, Toledo, Ohio, to engineer and provide working drawings for a landfill to be established utilizing #6 quarry. An application with all pertinent data was submitted to the state of Ohio. In due time a license was issued by the Ohio Department of Health (licensing is now handled by the Ohio Environmental Protection Agency). Application was also made to the Lorain County Board of Health, and a license was issued without delay. We were quite pleased with the progress to this point, but we knew we had a final step to take—that of obtaining a change in the zoning regulations of Amherst Township.

Although the zoning law provides for a Zoning Board and a Zoning Board of Appeals, the final decision is rendered by the township trustees. In Amherst Township we were faced with two trustees who apparently worked together and a third who allegedly was uncooperative with his associates. It was quite apparent that if we were to be successful in obtaining a zone change, it would necessitate the complete cooperation of the duo.

Coupled with the township problem was one involving the village of South Amherst. Although the quarry hole we proposed to use was in the township, the road to and from the site was in the village. In addition, many years ago the quarry company entered into an agreement with the village to allow the village to obtain raw water free from the premises. The water source was more than $\frac{1}{2}$ mile from our proposed landfill site, but we were unable to convince the townspeople that we would not pollute the public water supply. Although the village government could neither approve nor disapprove our venture, the village residents would be subjected to additional truck traffic, and consequently their views were entitled to be heard.

We met with the mayor and council of South Amherst in what turned out to be a rather harsh affair. At the conclusion of the meeting there was no question in our minds as to their feelings on the subject. In addition, we had a number of meetings with the two trustees involved. They

recognized that Lorain County did not have a satisfactory facility to accept and dispose of solid waste. They also recognized that we had a good site, a good process, and licenses from both the state and county. What they did not recognize was their opportunity to permit a service to the whole county. Unfortunately, if they made an unpopular decision, they could become quite unpopular themselves at election time. We failed to convince them of our case.

Although discouraged as a result of our failure to establish a solid-waste landfill for Lorain County, we have continued to try to develop a use for a large hole. We have talked with a company in the area as to the possibility of handling and disposing of some of the spent sand from their foundry. I am pleased to report that on this trip to the township trustees, we met little or no opposition. Having run a

representative sample through our laboratory, we were able to present to both the Ohio Environmental Protection Agency and the Amherst Township trustees adequate proof that the material we proposed to place in the hole was nontoxic in nature. We are currently negotiating with the foundry. We hope that in 10 to 15 years we will have one of several holes filled and one liability off our hands.

We don't think our experience with solid-waste disposal is uncommon. No doubt most households, including those of elected officials, set their trash out each week—and let someone else worry about its final resting spot. After all, they have more important things to worry about than where to put last night's newspaper. The hole is still there—it's still 75 acres in size—it's still 160 feet deep. Some day, some way, we're going to use it.

MEDUSA'S RECLAMATION PROGRAMS IN THREE STATES

by

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Medusa Cement Company
Wampum, Pennsylvania

ABSTRACT

Medusa Cement Company, a division of Medusa Corporation, is a medium-sized cement manufacturer serving the midwest, east, and southeast. Medusa's eight plants are located in Georgia, Pennsylvania, Ohio, Illinois, Michigan, Wisconsin, and Canada. Of these, six have active limestone, shale, clay, and sand quarries now in operation. This paper deals with the various individual state laws regulating mining and reclamation at the Georgia, Illinois, and Pennsylvania quarries. Several recommendations for future state mining laws are discussed also.

GEORGIA

Medusa owns and operates a cement plant at Clinchfield, Georgia, a rural area 30 miles south of Macon. The raw materials come from one limestone quarry next to the plant and two kaolin pits about 10 miles north.

In 1968 the Georgia Surface Mined Land Use Board, as a Division of the Department of Mines, Mining, and Geology, was created. The board is composed of three representatives of the mining industry, one from the Georgia Chamber of Commerce, and one each from the following five state agencies: Game and Fish Commission, Forestry Commission, Water Quality Control Board, Soil Conservation Service, and the Department of Mines, Mining, and Geology.

The Georgia Surface Mining Act of 1968 basically requires that mining operators reclaim annually as much land as they affect. Substitution of previously nonbonded mined land on an acre-for-acre basis is permitted.

Mining licenses are obtained by filing a reclamation plan for the land proposed to be affected, paying a license fee (which varies according to the number of employees at the quarry),

and posting a performance bond on the acreage to be affected (this bond averages around \$500/acre).

The reclamation plan is essentially left up to the operator to formulate; however, the state will provide assistance. Basically the law simply states that the mined land should be restored to a usable land surface by whatever earth movement, water impoundment, and planting are suitable. Reclamation plans must be approved by the board director, however, before a permit is issued. A land-use-plan map showing areas and acreages to be reclaimed, stripped, used for haul roads, or affected in any way must also accompany the permit application. This map should be accurate and must be revised annually.

Medusa is presently reclaiming by strategically locating spoil piles in areas where they can be blended into abandoned quarry faces when mining ceases. The overburden in the limestone quarry consists mostly of fuller's earth, which does not readily support vegetation; therefore the top strata of red clay must be saved and replaced on top of the spoil areas. Spoil-pile banks are limited to a 1:3 slope to reduce erosion and increase the chances for grass germination and maturation. Plans are also being made to reforest the area with fast-growing pines.

The kaolin pits are stripped from west to east, with the spoil gradually being blended into the mined areas. The red clay surface strata

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will be replaced here also, with the area taking on the look of a low wide depression which will not impound water.

ILLINOIS

The state of Illinois requires a surface-mining permit of all operators who disturb more than 10 acres or who mine areas where the overburden exceeds 10 feet. Medusa's plant in suburban Dixon, Illinois, has a limestone quarry and a sand quarry. The sand pit does not require a permit, as less than 10 acres are disturbed annually, and there is little or no overburden. The limestone quarry, however, affects 8 to 16 acres annually and has overburden which ranges from 5 to 55 feet in thickness.

Stripping is done by sidecasting or contour stripping with a Manitowoc 4500 dragline, and the spoil is deposited in windrows in the previous cuts. Until recently the only reclamation required was to strike off the tops of the piles to a 15- to 20-foot width and to do some "approved planting."

Mining is permitted (in most cases) within a short distance ($1\frac{1}{2}$ times the height of the high-wall + 10 feet) of roads and streams; however, reclamation in these areas must be to a near-original contour condition.

Under a revised law continuous reclamation is now required, along with concurrent backfilling to the inspector's approval. Reclamation should be completed within three years from the time the land is originally affected.

Mining permits are obtainable from the Land Reclamation Division of the Department of Mines and Minerals in Springfield and run from July to July of each year. The fee is \$50 plus \$25 for every acre of affected land. Bonding of the operator is mandatory and averages about \$1,000 per acre of affected land. The permit application requires information on the mineral deposit, the surface-mining technique and method, the pre-mining character of the land, drainage, roads, utilities, buildings, and land ownership, as well as a complete plan to reclaim the proposed affected land, including planting plans.

A copy of the reclamation plan and land-use map must also be filed with the county clerk of the appropriate county and be available for public inspection and comment for a period of 25 days. The reclamation plan cannot be approved during the 25-day period.

Reclamation regulations have changed during the past few years. Final restoration must now leave no more than a 15 percent grade, unless proof can be shown that a steeper grade can ac-

cept vegetation. Runoff water must be impounded and treated if necessary. Gob piles must be covered with 4 feet of soil that will support vegetation. Haul roads, ditches, treatment ponds, etc., must all be reclaimed within the law. All of the grading requirements must be met within three years of the end of the permit year, if substitution is not approved, and planting must be done with "approved" seed or planting stock. There must be a 65 percent stand in the fall following planting and an 85 percent stand after one year.

Prior to September 1 of each year, the operator must furnish to the Department of Mines and Minerals a map showing the area and acreage that was affected during the preceding permit year. This map must be accurate and must show the areas affected on a year-to-year basis.

PENNSYLVANIA

Pennsylvania has by far the most complicated law that we are affected by. There are two basic permits that must be obtained for each operation: first, a mine-drainage permit, which covers stream and discharge quality, and second, a mining permit. Each company in the state is also covered by a mining license, from which the mining permits are derived.

Unlike Georgia and Illinois, Pennsylvania permit applications are scrutinized by an office in Harrisburg. The people in this office have never been to your operation and are totally unfamiliar with its methods and problems. Permit applications generally require up to two months for action, and water permits require up to a year. One of our current water-permit applications has been in process for 15 months. Delays of this kind are unnecessary and add additional problems to the many a company already contends with.

Pennsylvania, in contrast to Illinois and Georgia, does not require a rigid complete reclamation plan with plans for planting with the mining-permit application, nor do they require concurrent reclamation within a given time limit. Pennsylvania allows the operators to set their own schedules, prodded only by the bonds the state holds; owing to a higher-than-50-foot highwall, the bonds for Medusa property are \$1,000 per acre, which is generally three or four times the value of the land.

Mine-drainage applications, which cost \$25, require information regarding mine location, type of mine, drill-hole data, water accumulation and treatment, stream relocation, mine development plans, local strata, backfilling, reclamation, public water supplies in the area, local wells, and settling basin plans. Certifica-

tion by a Professional Engineer or Registered Surveyor as to map and plan accuracy is also required.

Mining-permit applications require drill-hole data, backfilling and water-handling proposals, consent of surface landowner on a notarized form, and surety bond or collateral, along with mine location and acreage plotted on maps. The cost is \$300 per license per year with no charge for amendments to the license permits.

Medusa currently has four separate operations in Pennsylvania: two at Wampum, one in York, and one in Mt. Holly Springs, south of Carlisle.

The coal strip operation at Wampum is currently inactive and has been completely reclaimed by the original-contour method. It will be planted this spring (1974) with brome grass and alfalfa. The topsoil was saved and replaced after grading; the pH (7.2) was no problem.

The limestone operation at Wampum is active and produces about 900,000 tons of limestone, 100,000 tons of shale, 20,000 tons of coal, and 10,000 tons of underclay annually. Currently up to 250 feet of overburden, containing some coal, is being stripped to remove 22 feet of limestone. No acid-water problems from the coal seams are encountered because of the lime-water neutralization in the stone quarry below. There has been no finished reclamation in this pit as yet; however, backfilling is done concurrently with mining, and rough grading is constantly being done. Eventually the area will be hillside pasture at near-original contour with some terracing. The topsoil is being saved for future use in reclamation. The planting must meet the requirements of a state forester and display a "good" catch. The surety bond is released incrementally after backfilling and approved planting.

The York operation is an open quarry which will encompass an area of approximately 150 acres and be 150 feet deep when completely worked out. Little or no clay overburden is present; what clay is present is used as a raw material. The quarry will eventually become a lake, with the highwalls shot in on a slope and with grasslands around it. A multiflora rose hedge which completely encircles the property to a height of 7-10 feet acts as a visual screen. Again, owing to highwall height in excess of 50 feet, the bond is \$1,000 per acre. Obviously, the resulting lake would not require \$1,000 per acre to reclaim by flooding.

The Mt. Holly Springs pit, located at Toland, Pennsylvania, is one of the largest scars on our record. Purchased in 1971 from the Philadelphia Clay Company, it has a highwall of over 700 feet

of broken and fractured quartzite with little hope of ever holding a vegetative cover. The stripped overburden is deposited in enormous spoil piles and capped with waste clay. These piles eventually will be graded to a 30-degree slope and planted. The pit is currently expanding to the north, and spoil from that area will be deposited back into the old pit. Hopefully this will improve the area somewhat. Currently, white clay of unusually high quality is mined there.

CONCLUSIONS AND RECOMMENDATIONS

There are differences between the surface mining and reclamation laws of various states. The differences lie in bonding, fees, period between mining and completion of reclamation, plans required with permit applications, buffer zones, and renewal times.

Some personal suggestions are:

1. Application fees should depend on the acreage to be affected, as in Illinois, with a minimum charge to cover administration costs. This will not penalize the small operator or offer cheap permits to the larger operator, who requires more of an inspector's time.
2. Bonding should be at a rate concurrent with the costs of restoring the land after mining to a usable condition. The rate should not depend on the actual cash value of the land.
3. Reclamation laws should not require companies to put land into a better condition after mining than it was before.
4. Substitution of lands to be reclaimed should be allowed on a one-for-one basis.
5. Buffer zones between mining areas and houses, streams, property lines, and roads should be rigidly enforced. Suggested distances would be dependent on geologic conditions: property lines, streams, and roads—100 feet; houses—300 feet. In addition to these minimum barriers, a distance of 80 percent of the maximum depth of the quarry or height of the spoil pile should be added. This would allow for the caving of the quarry face or the terracing of the pile to a maximum angle of 35 degrees.
6. All topsoil should be removed and saved in a separate pile and should be replaced after rough grading.
7. All gob piles and slurry basins should be covered with a material suitable to support vegetation and vehicular traffic.
8. All water discharged from the mine site should be at least equal to the quality of the run-off prior to the inception of mining.
9. Backfilling should be done concurrently with mining, and reclamation should follow with-

in a reasonable length of time, which may be negotiated.

10. Reclamation plans should accompany the original permit application and contain, along with areas and types of reclamation, schedules and specific time limits, planting plans, and a long-range general mining plan.

11. All permits should be on a year-to-year basis, renewable annually. Reclamation plans could also be amended at this time.

12. Core-drilling results should be confidential, but available for inspection by the agency regulating the reclamation program.

13. A map should be kept up to date showing affected areas, haul roads, drainage, property lines, adjacent property owners, houses, wells, roads, future areas to be affected, and topography; the map should be at a reasonable

scale to show detail.

14. Permits should be able to be extended and amended quickly and conveniently, if needed.

15. All reclamation should be done to the approximate original contour or other acceptable form. Plans must be made to reclaim deep pits by some method (lakes, landfills, etc.).

16. An independent appeals board should be set up to dispose of problems resulting from the law. The board should be made up of mining industry personnel and state people (geologists and engineers, no politicians) in equal numbers and with results binding.

17. Mining-permit applications and amendments should be scrutinized by the applicable mining inspector, as he is most familiar with the ongoing mining process and with local conditions.

CONVERSION FROM QUARRYING TO UNDERGROUND MINING

by

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ABSTRACT

Zoning and environmental restrictions on land usage now make open-pit quarrying more and more difficult, especially near urban areas. One option for quarry operators is to go underground for mineral production. While underground-mining costs are higher than those for open-cut work, there are several compensating advantages. In many cases it is possible to produce the same material underground without affecting land values, and the surface is preserved for industrial, residential, or agricultural purposes. Proper planning can yield underground sites which have great potential value for industrial plants, warehouses, or other business uses. It is essential to plan underground mineral extraction using a three-dimensional modular-room architectural concept to fully exploit secondary space utilization. Prior to the start of underground mining an operator must make a careful geological engineering study to determine the suitability of the deposit and must prepare a plan for safe and economical mining for the purpose of converting to secondary usage.

INTRODUCTION

Healthy growth of urban and suburban areas requires adequate supplies of mineral aggregates within the immediate vicinities. Some communities have experienced difficulties in obtaining low-cost aggregates because potential deposits have been built over or zoned out of consideration by rapid urban sprawl. In many cases, established quarries have been squeezed out of business by a variety of factors. Thus the only option commonly left to mineral suppliers and contractors is to haul in aggregates from distant locations, a recourse which increases construction costs.

It is important for communities to locate and develop their mineral aggregate deposits before the sites are utilized for other purposes. Logical zoning restrictions should be developed which will allow for the orderly development and utilization of potential construction materials. Once the surface above an aggregate deposit has been built over with houses, shopping centers, or other commercial buildings, that aggregate

source has been lost to the community.

RESTRICTIONS ON QUARRYING

Quarrying or open-pit mining of mineral aggregates is becoming more and more difficult because of the many restrictions that have been imposed on such operations in recent years.

The last five years has been an era in which the public has become very conscious of the environment. This awareness of a need to clean up the land has led to restrictions on land use and regulations on industrial activity. The desire to keep things in a "natural" state is not always compatible with the economic growth of a community. In their haste to clean up the environment, community leaders have often overreacted and passed laws which prohibit the best use of their resources. Like it or not, the mineral aggregate industry has to accept the fact that it will have to live with zoning and environmental constraints.

To the public a quarry is an eyesore. Besides

gouging a hole in the land, quarries with their mining operations and milling plant are unsightly, noisy, and dusty. The adjoining landowners are convinced that the blasting operations, which they can hear, are causing damage to their homes. Thus quarries are not considered assets to communities because they are not aesthetically pleasing.

With the present mood of the public, open-pit mining of mineral aggregates in urban or suburban areas will become more restrictive. Quarry aggregate producers will always be scrutinized intensively for any possible violations of environmental codes because their operations are in full view of the public.

GEOLOGICAL AND SITE CONSIDERATIONS

Not all quarries can be converted to underground mining of the aggregate. Geologic conditions will dictate whether a specific quarry can be transformed into an underground operation. Therefore it is extremely important to make detailed geologic evaluations prior to any decision to abandon open-pit mining for underground extraction of aggregate.

Preliminary assessment on the feasibility of going underground can be made from a topographic map of the area. Conventional, U. S. Geological Survey topographic maps contain information on landforms, streams, surface drainage patterns, and topographic relief. These maps also show cultural data such as highways, utilities, buildings, and railroads. The accuracy of the cultural information will depend upon the date the maps were issued.

Specific geology of the area can be obtained from state geological surveys. These agencies have geologic maps, well logs, and descriptions of the rock units from which to evaluate the geology of the site. In addition, most surveys will make on-site appraisals of the geological conditions if requested.

Feasibility studies should include assessments of the overburden (the soil material above the rock), physical properties of the rock units, rock structures, chemical properties of the rock, surface- and ground-water conditions, and accessibility to transportation. The last is important to the type of industrialization that is planned for the mined-out space.

Much information on the overburden, rock units, and drainage can be accumulated from on-site examinations of the land surface, quarry face, and nearby roadcuts or exposures. The quarry faces will yield the best information on lateral and vertical changes in the character of

the rock. From face examinations information can be obtained also on rock structures and variations in overburden thickness. Supplementary core drilling is mandatory to further delineate subsurface conditions in the proposed mine-site area. If no quarry exists, all initial design parameters will have to be determined from core drilling.

The overburden has very little strength for supporting mine openings, but it constitutes a load on the roof rock. Character of the overburden influences surface- and ground-water movements. Porous sandy material will allow surface water to infiltrate downward, whereas clayey deposits will inhibit infiltration and cause the water to surface-flow off the site. The overburden also will influence transportation planning, slope stability of open cuts, and surface development.

It is impossible in a survey paper to discuss adequately the importance of the physical properties of the rock units to the design of underground mines. For mining aggregates underground it is imperative that the roof-pillar configurations be self-supporting and have infinite stability. Competent rock-mechanics analyses are a must for a successful venture. Rock properties that require evaluations are compressive strength, tensile strength, Young's modulus, porosity, and permeability. All shales should be tested for moisture durability. Specific considerations of roof and floor rock will be discussed later in the text.

The structural properties of the rock forming the roof, pillars, and floor of the mining area must be considered for stability and mine-plan purposes. In most cases the rock units in which industrial developments are made are sedimentary rocks. Because sedimentary rocks exhibit bedding, several stratigraphic-structural parameters must be studied. Bedding planes vertically separate a sedimentary-rock sequence into individual units of varying thickness and composition. These separations constitute planes of weakness that may be used to establish the unit to be mined and the roof and floor boundaries. From the stability standpoint, the more pronounced the bedding and the thinner the beds, the greater the possibilities of roof problems, especially if numerous shaly beds are present. Special care must be taken to delineate thinning or lensing out of beds and to map facies changes within a layer.

Although sedimentary rocks are generally considered to be flat lying, they commonly have a gentle to moderate dip. The attitude of the beds and any local folding must be identified in order to best plan the overall mine workings.

Faults, joints, and solution zones can cause support problems. Unless they are numerous,

these structures can be designed for by modification of the rooms and pillars to prevent long continuous exposure in a roof or by leaving these areas unmined.

Mineralogical and chemical analyses should be made on the rock units to be mined out and on those units forming the roof and floor. These data can be used to complement the physical-property data and also to evaluate chemical reactions detrimental to rock durability or harmful to stored commodities.

Any site study must consider surface- and ground-water conditions. Adequate provisions for channeling away surface runoff are a must, otherwise this water could infiltrate the mine via solution channels or construction openings. The water table and the ground-water flow must be established and potential leakage zones investigated in detail prior to mining. If leakage is expected to occur in the mine, the water should be chemically tested for corrosiveness and other harmful properties. Wet mines should be avoided for industrial usage because of the multitude of problems they create.

Of prime importance to any conversion of a quarry to an underground operation in which industrialization is planned subsequent to mining is adequate access of the mine to transportation. An ideal site will permit both a railroad spur and a truck entry into the mine. Such developments decrease handling and transportation costs. In preplanning secondary use of an underground-quarry aggregate site the developer should consider a number of options relating to transportation, space usage, and dockage. For interstate commodities a railroad spur to the site offers distinct promotional advantages. For localized or certain types of industrializations truck entry alone may be sufficient. Previous experience has shown that the combination of rail and truck accesses to underground industrial developments gives the most flexibility to changing markets and site usage.

DESIGN AND OPERATION OF UNDERGROUND MINES

Underground quarrying for limestone to be used for aggregates, cement, and lime is being successfully carried on in many locations in the central states. In Missouri, which is probably the leader in this type of mining, some of the best examples are the Mississippi Lime Company, of Ste. Genevieve, which produces limestone from underground stopes 90 feet in height, the Kansas City mines, which produce the Bethany Falls Limestone from faces only 12 to

14 feet high, and Missouri Portland Cement Company, which produces its stone from an intermediate height. Several other examples could be selected from Missouri, Illinois, Tennessee, Kentucky, and Ohio, where economically profitable underground stone operations are producing stone from formations of widely differing thickness.

The ideal position for making an entry into an underground mine is from an existing quarry face; in this case, the process of converting from open quarrying to underground mining is not a difficult one. The portal locations should be properly located with regard to surface accessibility by various types of transportation as well as permit the best relationship to the subsurface workings. A minimum number of entries should be employed to facilitate ventilation and to permit the best design for secondary usage of the worked-out area. Proper face preparation is essential before the entries are driven to prevent future rock slides or falls at the portal.

The first step in the design of an underground mine is the determination of the mining zone. This will require (1) selection of the best zone of recoverable stone, (2) selection of a competent immediate roof rock, (3) assurance of a sufficient thickness of total roof rock, (4) design of stable pillars, and (5) selection of a strong floor rock. All of these requirements must be met if the mine operation is to be successful, but to meet them may require some sacrifices in recovery. In open quarrying it may be possible to recover all of the stone of a suitable geological section. The above requirements probably will reduce the recoverable strata thickness and will require that a percentage of the mined section be left in place as permanent support pillars. The selection of the best zone of recoverable material can be determined from core samples and quarry-face examination, considering the above five requirements and the continuity of the zone.

To accommodate secondary usage a mine should be designed to have the maximum usable space and to have the minimum conversion cost to industrial space. This may require a mining plan which is somewhat more costly and which may have slightly lower recovery than a mine which is designed only for stone production. However, the higher costs of development and mining are offset by the lower conversion costs when the space is prepared for secondary usage; fewer walls will have to be constructed, space will be more efficiently used, and other efficiencies will be realized. In the following discussion of the requirements of the mining zone and other mine-design problems, some of these modifications for secondary usage will be men-

tioned.

The immediate roof should be a massive bed free of joints or other structural defects and continuous over the area to be mined. A roof rock which thins or lenses out probably will lead to serious support problems later. The required thickness of this bed cannot be given empirically, but rather is a function of its physical properties, of the depth of overburden, and of the nature of the superimposed roof rocks. If the superimposed rocks are of good quality and are well bonded across bedding planes, the critical thickness of the immediate roof bed can be less than a foot. A much greater thickness of competent stone is needed to form the immediate roof if the superimposed beds are very thinly bedded, shaly, or fractured. As the unsupported cavity span is widened, a greater slab thickness is necessary. Under some conditions rock bolts can be employed to give additional strength to bedded rocks. As good roof conditions are essential for long-term roof stability, conservative practice must be employed. Extreme care must be taken in drilling and blasting to avoid fracturing of the roof rock. A combination of rock-mechanics calculations and an analysis based upon mining experience can provide the best answer to the roof problem.

The selection of a floor rock generally is not difficult; however, it is essential that a stable floor be provided. A shale floor or a shale bed a short distance below the floor may create problems. Upon exposure to moisture and the action of haulage and loading equipment, a shale floor can be worked into a quagmire. Shale may yield when a pillar is loaded above the bearing capacity of the shale. Also shale can take on water and swell, causing the floor to rise around the pillars. Because of the above problems a protective zone of more stable rock should be left above shale.

In many limestone mines the objective in production was maximum recovery at minimum cost. This commonly resulted in random pillar arrangement, excessively wide room spans, pillars which were too small, fractured, or poorly located, bad roof conditions, soft shale floors, insufficient cover to support surface structures, etc. In some cases additional rock was recovered before abandoning an area by taking down additional roof, taking up floor rock, or robbing pillars. In a few places these practices have resulted in roof failures and surface subsidence. Even if subsidence does not occur, hazardous underground conditions make the mine completely unsuitable for any secondary usage. Where surface subsidence occurs, the value of the land is severely depre-

ciated. In many cases no commercial or residential use can be made of the surface because of the hazard of future subsidence.

Room and pillar dimensions can be determined by an engineering analysis of the physical properties of the rocks combined with the size of openings needed for an efficient and economical mining plan. Additionally, if the mine is to have a secondary industrial usage, conventional mining practices may be modified to provide the maximum economy and convenience in the space created. In the initial geological engineering studies, samples of the rock in the roof and mining zone would be tested to determine their physical properties, including compressive strength, Young's modulus, and tensile strength. Using these values along with thickness of overburden and mining height, a theoretical determination of roof span, percentage recovery, and pillar dimensions can be made. These can then be modified to allow for the nonuniform conditions existing in the rock, and for the practical considerations of space usage.

Most mines designed for the production of stone will be at shallow depths, therefore the burden on pillars will not be great. (As an approximation, it may be assumed that the pressure exerted by the overburden will be one pound per square inch per foot of depth of the overlying material; thus at a depth of 100 feet and with pillars occupying 25 percent of the mining area, the

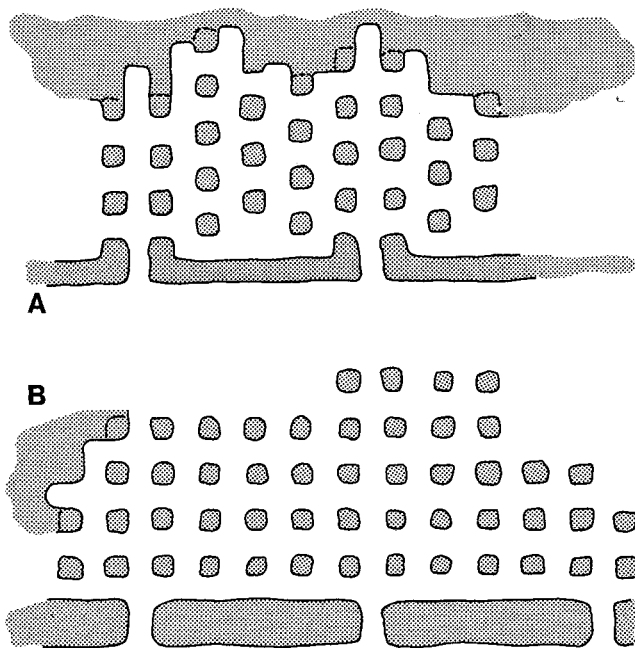


FIGURE 1. - Mining plans. A, staggered pillars, B, aligned pillars.

pillars have an average vertical stress of 400 psi, which is only a small percentage of the compressive strength of the average limestone.) It would seem that a very small pillar area is all that is needed for support, but owing to non-uniform conditions, blast fractures, stress concentrations, and the possibility that extra loads may be superimposed by the construction of surface buildings, maximum recoveries of 75 to 85 percent are recommended.

After determination of the percentage of the area to be left as support pillars, dimensions of the pillars and openings can be established by considering the safe and efficient use of mining equipment and secondary usage of the space. Systematic room and pillar arrangements should be selected in favor of random pillars, which have been used in unplanned operations. Typical mining plans illustrating staggered and aligned pillars are shown in figure 1. Arguments can be presented in favor of staggered pillars; however, linearity is a property required for space utilization, therefore pillars which are aligned in both directions are preferred. Where the space is to be used for industrial purposes staggered pillars present obstacles to efficient arrangements of machinery for manufacturing, and material-handling problems are multiplied. Staggered pillars also make it much more difficult to provide ducts and piping that are required for atmospheric control and utilities. Pillar patterns should be aligned so that the rooms will accommodate continuous machinery arrangements.

Although square or round pillars can be used in linear patterns because they satisfy good mining practice, they are not the most economical pillar system for conversion of space to secondary industrial usage. Compartmentalization is a necessity for either manufacturing or warehousing. Partitions are needed for simultaneous occupation of the space by different tenants. Also the same tenant may require multiroomed space for his operation. Factories generally require rooms to be separated for various reasons, and warehouse-storage complexes handling different commodities will require compartmentalization. When square or round pillars are employed, compartments are made by constructing walls of concrete block or other fireproof material. Such construction not only adds to the cost but generally is not as satisfactory as a natural rock wall. This is particularly true where a room is to be refrigerated or requires precise control of temperature or humidity. Elongated continuous pillars (rib pillars) can provide the lateral boundaries or walls of small rooms which con-

tain no intermediate pillars. Where larger rooms are required the rib pillars can be spaced more widely and the central area can be supported by smaller pillars arranged in a linear plan (fig. 2).

The haulageways for rail or truck generally should be normal to the long axis of the rib pillars and would be bounded by continuous pillars, thus forming a skeletal structure (fig. 2) that might be likened to the ribs and breastbone of the human body or to the rafter-and-purlin structure of a roof.

In a gently dipping deposit, the haulage entries should go updip from the portal. The rib pillars which form the long sides of the rooms would then parallel the strike. Based upon stress analyses linear supports on the sides of the rooms and those bounding the haulageways would provide good stability and would permit wider spans than would discontinuous small pillars.

Generally rib pillars would intersect any joint systems and could be oriented to do so. Should a joint be encountered within a room, supplementary support by rock bolts or bolts and channel iron could be provided. This type of support could also be applied at the intersections where the rib or boundary pillars would be penetrated to gain access to a room. However, with good roof rock and proper span selection, there should be little need for other than pillar support. In good massive limestone formations, 60-foot-wide rooms and 25-foot-wide rib pillars are feasible. In weaker formations room spans should be reduced to 30 or 40 feet. If large rooms bounded by continuous rib pillars are internally supported by shorter linear pillars, as in figure 2, the spans would be somewhat less than with continuous pillars, owing to the longer diagonal spans across intersections between pillars. A large number of room arrangements and dimensions are possible.

The actual mining can be carried out by a variety of procedures and with a wide choice of mining equipment. It is doubtful that rail haulage would be considered in any operation except one with very long hauls. Belt conveyors can be employed also, but as most stone production is performed on a single level, the movement of the broken material can be best performed by trucks carrying it from the working face to the exterior dumping point or by load-haul-dump (LHD) equipment, which can perform these three functions with but a single operator on one piece of mobile equipment. With LHD equipment there is, from the face to the dumping point, a maximum distance, ranging from 1,000 to 2,000 feet, beyond which such equipment is no longer economical. These units are most efficient when the haul distance is 500 feet or less.

Stone may be drilled and blasted on various

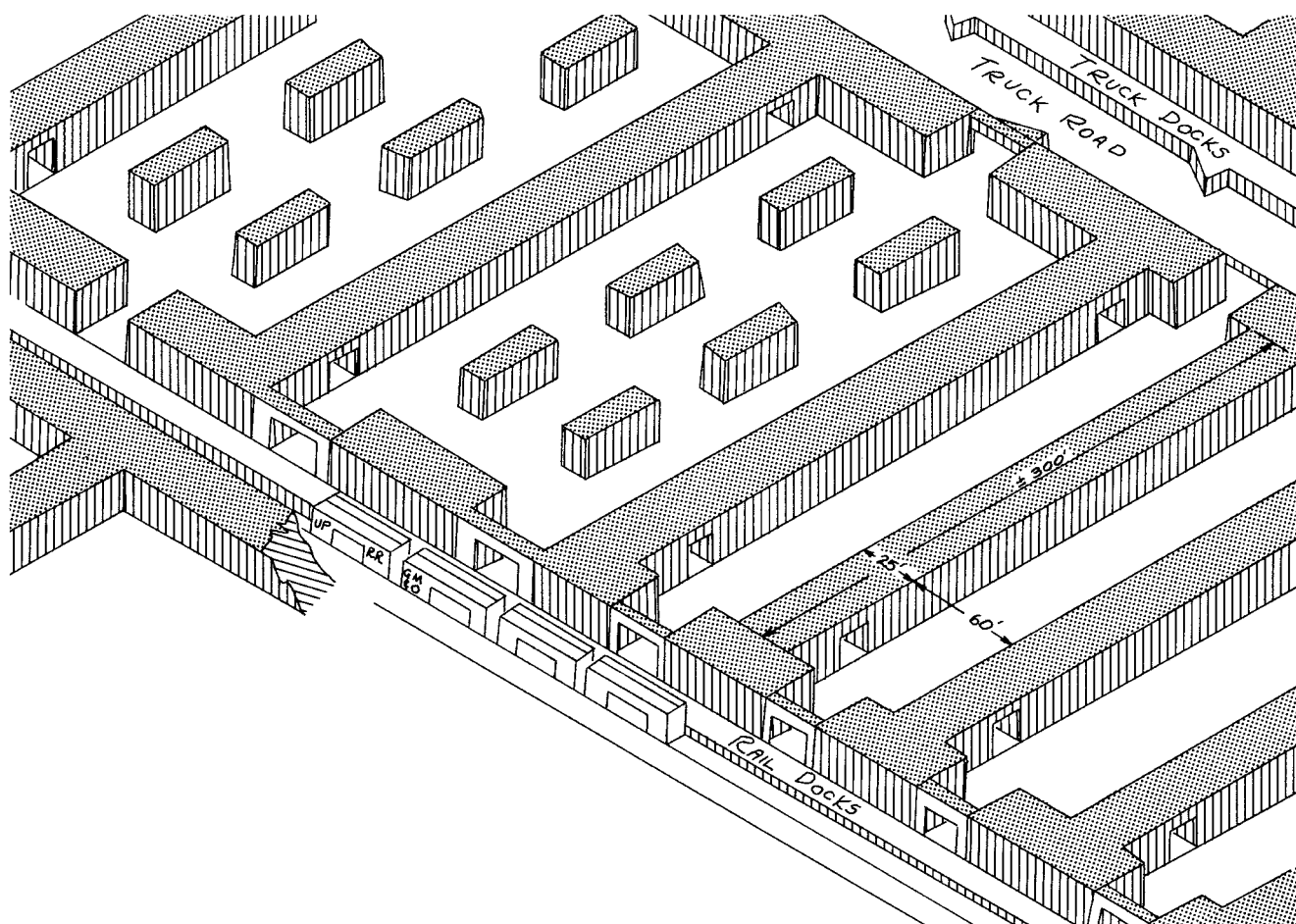


FIGURE 2. - Compartmentalized mine adapted to industrialization.

face plans. Faces up to 25 feet in height may be drilled in a full-face advancement system (fig. 3A) using mobile jumbo drills. Where the mining zone is thicker than 25 feet it must be broken in two or more sections. The most common method is that of advancing abreast or heading at the top of the ore zone, then breaking the remaining bench as the second stage (fig. 3B). The bench may be drilled with vertical or inclined downholes, using mobile drills. A third possibility places the heading at the bottom of the mining zone followed by breakage of the upper rock using drills from an elevated platform (fig. 3C). A fourth method is a modified shrinkage stoping system (fig. 3D) in which the lower stone is broken first, then additional ground is broken by drilling from the top of the muckpile formed by the first blast. Each blast is followed by barring down the back, leveling the muckpile to the desired height, then drilling and blasting; this process continues until the final back is reached. This method is labor ex-

pensive and has fallen out of favor with mine operators.

CONVERSION OF MINED-OUT AREA TO INDUSTRIAL SPACE

The space created by underground mining can be converted into valuable industrial space. This can be done after the completion of mining, or it can be started as soon as sufficient area has been established and vacated, while mining continues at a safe distance. The conversion process may involve some or all of the following, depending upon the purpose to which the space is put: (1) truck and/or rail docks, (2) drainage and seepage control, (3) heating, (4) dehumidification, (5) refrigeration, (6) lighting and power, (7) floor finishing, (8) wall and roof painting, (9) fire-control systems, and (10) roof support where required.

In general, the costs involved in the prepara-

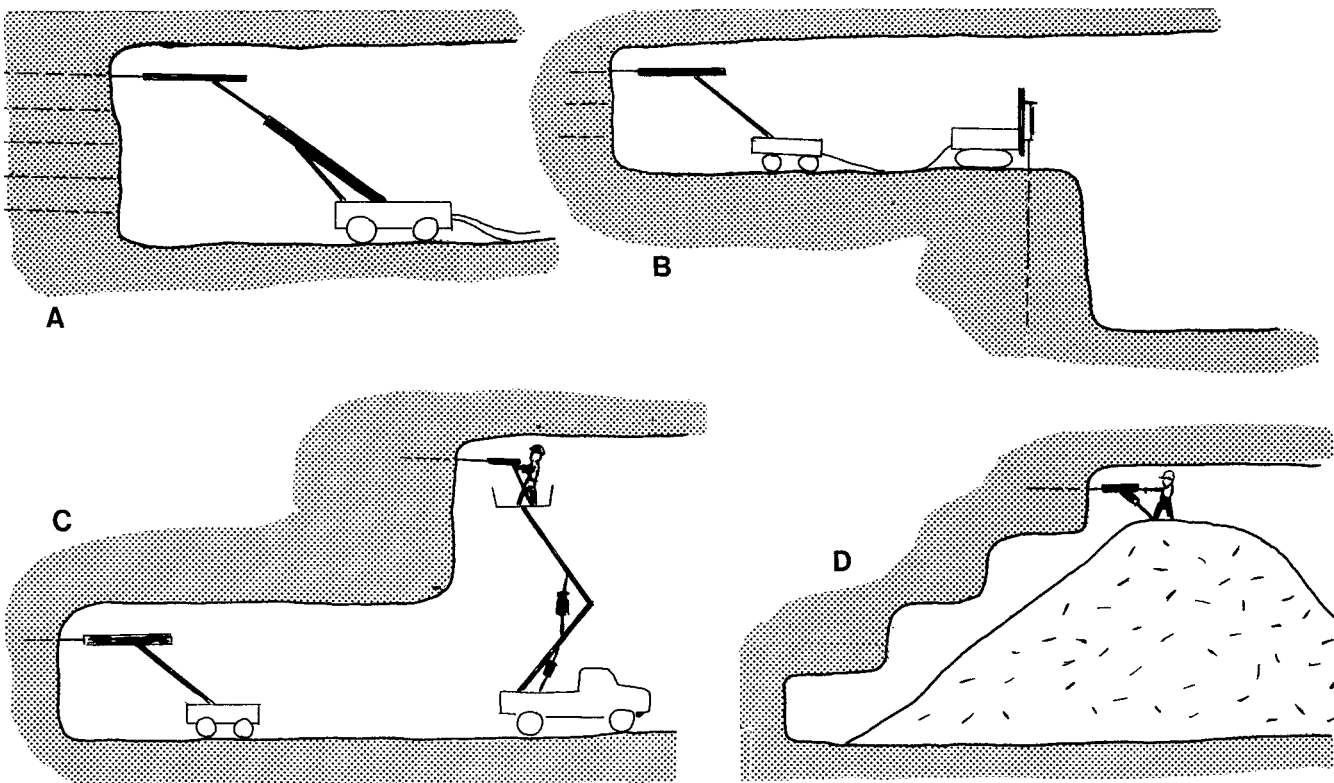


FIGURE 3. - Mining methods. A, Full face mining, B, top heading and bench method, C, bottom heading method, and D, shrinkage method.

tion of industrial areas underground are less than those in above-surface structures; where a mineral product pays the cost of the raw space, only the conversion expense remains. The operational and maintenance expenses of the completed space ordinarily will be far less than for a surface plant.

As a rough example of space cost, assume an underground limestone mine with a mining height of 20 feet, compared with a surface structure providing similar headroom. At a mining cost of \$1.00 per ton, the cost of the raw space would be \$1.50 per square foot of floor space. The conversion costs, including floors, lighting, drainage, air conditioning, sprinkler system, etc., will average about \$6.00 per square foot. This amounts to a total of \$7.50 per square foot for a completed 20-foot room. If all of the finishing details were not required, this cost would be less. One survey (The Harbinger, 1971) indicates that the average cost of conversion from mined area to warehouse space was \$3.00 per square foot. The profit of the limestone produced and sold should be deducted from the \$7.50. A cost figure sometimes used for above-ground factory or

storage structures with similar provisions is \$1.00 per cubic foot. Costwise this amounts to \$20.00 per square foot for a room 20 feet high.

One underground-warehouse operator stated that his annual cost for heat, light, and air conditioning was less than \$0.06 per square foot. The natural fireproof construction plus freedom from storm damage and other surface hazards brings insurance rates far below those for similar operations on surface locations.

ADVANTAGES TO LOCAL COMMUNITY

Mining stone in a planned manner to assure long-term stability of underground openings has distinct advantages for the developers and the communities. During the mining process the local contractors will obtain cheap new stone for building purposes, thus lowering construction costs for roads, buildings, etc., within the community. After mining, secondary development of the space will provide industry for employment of the local people. Since the industries will be underground there are no unsightly buildings and storage areas readily apparent to the eye. Trans-

portation to and from work can be minimized, as the employee can literally "live on top of his employer" if residential areas are developed on the surface.

A hidden asset which has not been recognized by local governmental officials is the literal doubling of the tax base because of surface residential or commercial structures superimposed on underground industrial properties. This concurrent use of the surface and subsurface has been termed the three-dimensional concept of land use.

SUMMARY

Restrictions on land use, especially for open-cut mining, make it desirable to go underground for mineral production in many areas. This is particularly true of limestone mining near metropolitan districts, where the noise,

dust, and unsightliness of an open-pit mine or quarry arouses opposition to this type of land use. In many cases it is possible to produce the same material underground without affecting property values, and the surface can be preserved for other uses.

Underground mining costs are higher and recoveries are lower than in surface mining. These disadvantages may be justified by lower land costs (the surface is not destroyed) and by secondary industrial development of the created space. Underground mining has several environmental advantages. Also there is the distinct advantage of an operation which can continue throughout the year without concern for adverse weather conditions. Economic analyses of open quarries versus underground mining, considering the points mentioned above, have proven that conversion from surface to underground production in or near urban areas is justified economically as well as environmentally.

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OVERVIEW OF USE OF CARBONATE ROCKS FOR CONTROLLING ACID MINE DRAINAGE

by

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ABSTRACT

Acid mine drainage is the result of the oxidation of pyrite and similar iron sulfide material and the release of iron and sulfuric acid into the environment. In addition to the acid water flowing from underground and surface mines, spoil materials in surface mines are acidic and will not support good vegetative growth; thus erosion is a major problem. Lime and limestone are the major neutralizing agents used to treat these acidic conditions. Lime is the reagent preferred by industry for treating acid discharges, although a few companies use limestone. Agricultural limestone is used to "sweeten" acid spoils.

INTRODUCTION

The mining of coal commonly results in the production of acid. Water discharging from underground and surface mines will have a low pH and undesirable concentrations of sulfate and aluminum, and of iron, manganese, and other heavy metals. Acid production also will cause the spoil material to be undesirable for establishing vegetation, which is the prime soil stabilizer to prevent erosion.

An estimated 160,000 kilometers (100,000 miles) of streams in Appalachia have been degraded by acidity (Appalachian Regional Commission, 1969). Acid problems in western Kentucky, Indiana, Illinois, and Montana also have been documented (Grubb and Ryder, 1972; Corbett, 1968, 1969; Orrin Ferris, Montana Department of Natural Resources and Conservation, personal communication, 1972). Copper, gold, lead, zinc, and other heavy metal mines also produce acid. A recent estimate (Hill, 1973) showed the total acid discharge to our streams from coal mines to be 3 million kilograms (6.5 million pounds) per day. As seen in figure 1, the acid discharge from active surface and underground coal mines should approach zero by 1977. This estimate is based on federal and state regulations requiring treat-

ment of all acid discharge from active mines by 1977. Abandoned underground mines are by far the major source of acid water. Only a small natural decrease in this source is projected. In order to accelerate this decrease, major technological and economical breakthroughs must occur, and massive public funding must be provided. Abandoned surface mines will correct themselves at a faster rate than underground mines. In addition, technology is far more advanced for controlling this problem. Most abandoned surface mines could be prevented from producing acid if sufficient funds were available for reclamation. Figure 1 assumes only a natural decrease in acidity and does not project a clean-up program by either federal or state governments. However, both governmental bodies have begun a limited cleanup of abandoned surface mines. The advent of technological development and strong surface-mining laws should result in only limited acid discharge from current and future surface mines as they are abandoned. No such technology exists for underground mines and we can expect the problem to get worse with time.

ACID FORMATION

Although the exact mechanism of acid-mine-

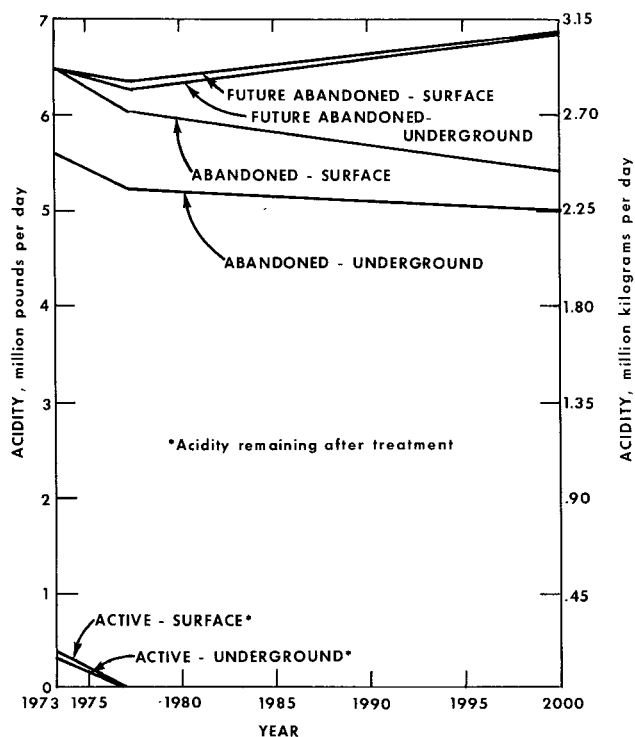
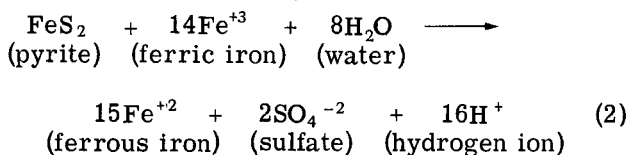
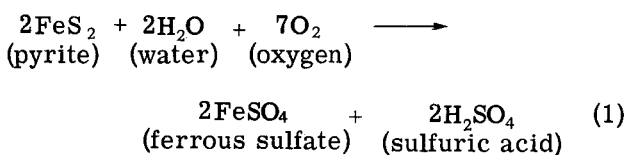
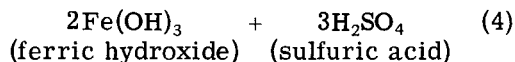
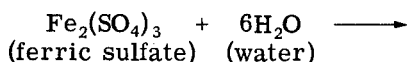
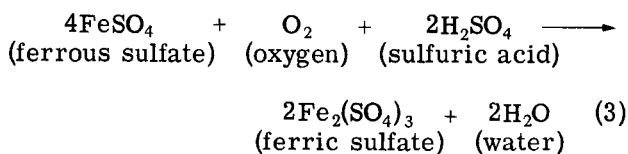


FIGURE 1. - Acid production from coal mines by source, 1973-2000.

drainage formation is not fully understood, it is generally believed that pyrite (FeS_2) is oxidized by oxygen (equation 1) or ferric iron (equation 2) to produce ferrous sulfate and sulfuric acid:



The reactions may proceed to form ferric hydroxide and more acid:



Water with low (2-4.5) pH is produced. At these pH levels the heavy metals such as iron, manganese, copper, and zinc, as well as calcium and magnesium, are more soluble and enter into solution to further pollute the water. Water of this type supports only limited water flora, such as acid-tolerant molds and algae; it will not support fish life. Such water destroys and corrodes metal piers, culverts, barges, etc., increases the cost of water treatment for power plants and municipal water supplies, and leaves the water unacceptable for recreational uses.

The amount and rate of acid formation is a function of the amount and character of the pyrite available, the movement of oxygen to the pyrite site, and the removal of the oxidation products from the site (Morth, Smith, and Shumate, 1972).

TREATMENT OF ACID MINE DRAINAGE

If all of the 3 million kilograms (6.5 million pounds) per day of acid being discharged to our streams were to be treated, over one million metric tons of carbonate rock would be required per year. In reality, only the active underground and surface mines are under pressure by state and federal laws to be treated at this time. The annual acidity load from active mines is approximately 205,000 metric tons (225,000 short tons) per year. An approximately equal amount of 100-percent-pure limestone would be required to meet this demand. Lime, not limestone, is the predominant neutralizing agent used by industry. In 1973, 41,600 metric tons (46,000 short tons) of lime were reported to have been used to treat acid mine drainage (Gutschick, 1974).

The neutralization process provides the following benefits:

1. Acidity is decreased and alkalinity is increased, thereby increasing the pH.
2. Heavy metals are removed. The solubility of heavy metals is dependent on pH; that is, up to a point, the higher the pH, the lower the solubility.
3. At higher pH ferrous iron, which is commonly associated with acid mine drainage, oxidizes at a faster rate to ferric iron. Iron is generally removed in the ferric form.
4. Sulfate can be removed if sufficient calcium ion is added to exceed the solubility of calcium sulfate; however, only in highly acidic acid mine drainage does this occur.

Some shortcomings of the neutralization process are:

1. Hardness is not reduced and may be in-

creased.

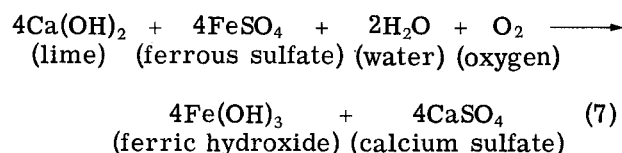
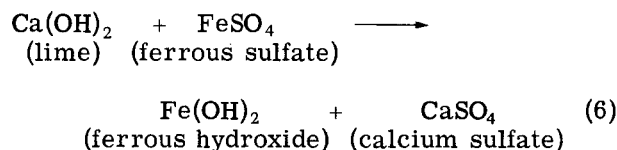
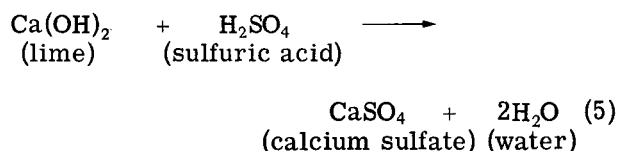
2. Sulfate is not reduced to a low level and generally exceeds 2,000 mg/l;

3. The iron concentration generally is not reduced to less than 3 mg/l;

4. A waste sludge is produced that must be disposed of.

LIME TREATMENT

The lime reacts with acid mine drainage as follows:

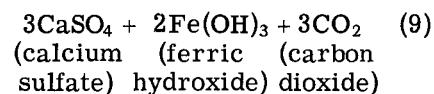
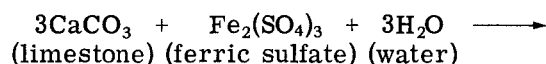
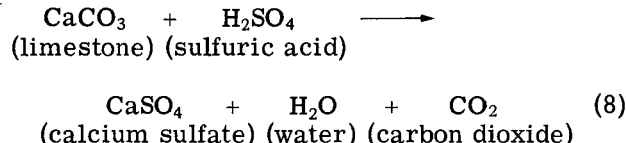


A typical lime treatment plant is shown in figure 2. Acid mine drainage is discharged from the mine directly to a rapid-mix chamber or to a holding/flow-equalizing pond, from where it flows to the rapid-mix chamber. Hy-

drated lime is fed to the rapid-mix chamber either as a slurry or dry. If the ferrous iron concentration is low (less than 50 mg/l), the water is treated to a pH of 6.5 to 8 and flows directly to the settling chamber. If the ferrous iron is high (greater than 50 mg/l), the pH is generally raised to a higher level (8 to 10) and then passed to an aeration tank, where the ferrous sulfate is converted to ferric sulfate according to equation 3. Then the water flows to a settling chamber. The settling chamber may be a clarifier, pond, or strip-mine pit. Here the aluminum and calcium sulfate, and iron and other heavy metals precipitate. The supernatant is the treated water. The precipitate or sludge is removed from the settling chamber and disposed of in a second pond, strip-mine pit, underground mine, or landfill. In some cases the pond serves as a settling chamber and for permanent storage of the sludge.

LIMESTONE TREATMENT

The limestone reacts with acid mine drainage as follows:



Although limestone is a cheaper reagent than lime and produces a smaller amount of denser sludge, the stone has not received wide acceptance because: (1) the carbon dioxide that is produced buffers the reaction, and it is difficult to raise the pH above 6 without using excessive amounts of material; (2) limestone is ineffective with high-ferrous-iron water; (3) the size, characteristics, and method of application of the limestone are critical; and (4) the system generally is more complex for limestone than for lime.

Several different treatment schemes have been utilized for limestone treatment (figs. 3, 4) (Hill and Wilmoth, 1971). The simplest method is the placement of limestone in a stream bed (fig. 3). The acid water is treated as the water flows through the bed. This method has proven

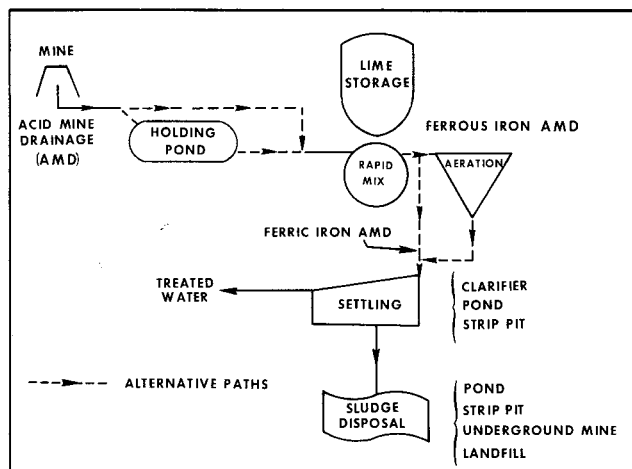


FIGURE 2. - Typical lime treatment plant.

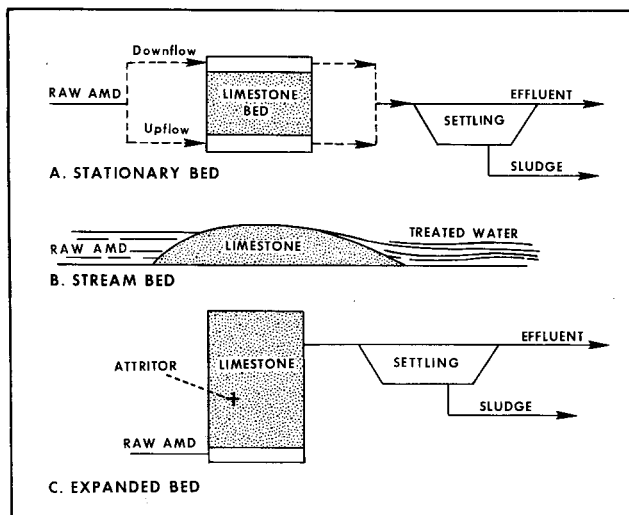


FIGURE 3. - Limestone treatment flow-sheets, limestone beds.

to be ineffective because the limestone quickly becomes coated with iron, calcium sulfate, sediment, and biological growth which prevent the acid water from dissolving the limestone.

An advancement of this scheme is the placement of the limestone in a tank. In this manner a smaller sized limestone can be used. The stationary bed is best operated in the upflow mode and with low-iron water. A modification of the stationary bed has been the placement of an attritor in the bed to help remove coatings. Part of the bed of stones can also be circulated through a pump. The pump serves to remove the coating.

A tumbler similar to a lime kiln also has been used (fig. 4). Pennsylvania State University has conducted extensive studies on this method (Lovell, 1973). The direct feeding of pulverized (200 mesh or less in size) limestone, in a manner similar to lime treatment, has also been evaluated (Hill and Wilmoth, 1971).

The utilization of limestone can be summarized as follows:

1. All of the limestone processes described are applicable to the low-iron acid-mine-drainage situation, with exception of the stream-bed method.

2. Expanded beds, tumblers, and pulverized-limestone systems are applicable to ferric iron acid-mine-drainage situations.

3. Above a ferrous iron concentration of 50-100 mg/l, limestone treatment does not appear applicable. Below this range, tumblers and pulverized systems with aeration are feasible.

4. For pulverized-limestone systems, the smaller the limestone particle size, the faster the reaction and the greater the utilization of the limestone.

5. An excess of 1.4 to 3.0 times the stoichiometric amount of limestone will be required.

LIMESTONE - LIME TREATMENT

The split treatment of acid mine drainage with limestone and lime may offer some advantages in cost and improvement in sludge characteristics. Such treatment might also be used on ferrous iron acid mine drainage. A two-step process is required. First, the acid mine drainage is treated with limestone to a pH of 4.0 to 4.5 to take advantage of the pH range where limestone is most effective. The water then passes to a second reactor where lime is applied to raise the pH range to the desired level. This process may have a cost advantage over lime alone and produce the desired sludge characteristics of the limestone process.

LIMESTONE TREATMENT OF SPOILS

Spoil accumulated during the surface mining

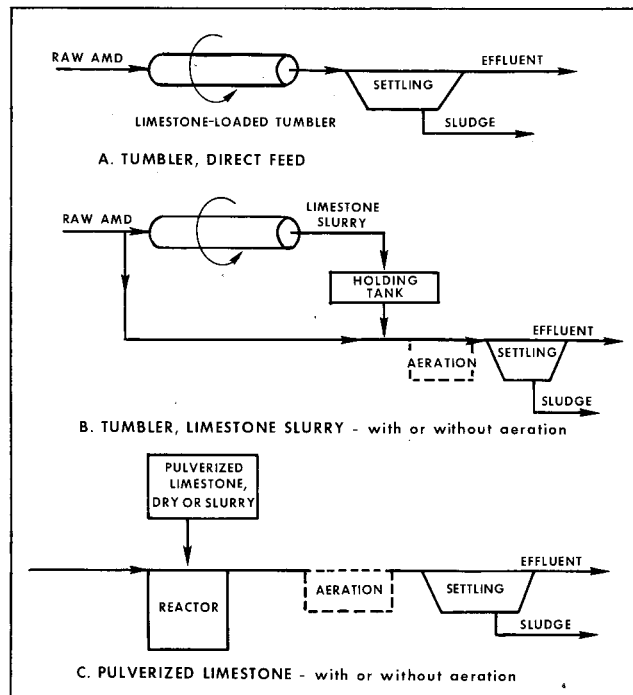


FIGURE 4. - Tumbler and pulverized-limestone treatment systems.

of coal commonly requires neutralization with agricultural limestone to raise the pH to an optimum level for vegetative growth and nutrient utilization. Even in the case where topsoil is removed before mining and then replaced, limestone is needed for best plant growth. The use of limestone in this case is similar to its use in agriculture.

The Kentucky Division of Reclamation (personal communication, 1974) reported that in western Kentucky between 10 and 27 metric tons/hectare (4 to 12 short tons/acre) of agricultural limestone are applied during reclamation. In many locations in eastern Kentucky limestone is not used. Limestone is commonly used in Pennsylvania and northern West Virginia. The general rate in northern West Virginia is 5 to 10 metric tons/hectare (2 to 4 short tons/acre).

Approximately 30,000 hectares (75,000 acres) of land are surface mined for coal each year. A

large portion of this land requires the application of agricultural limestone for optimum development of vegetation. If it is assumed that half of this area requires 10 metric tons/hectare (4 short tons/acre), then the annual demand for limestone would be approximately 150,000 metric tons (165,000 short tons).

SUMMARY

The demand for limestone and lime to neutralize acid mine drainage and surface-mine spoils is upon us. As federal and state discharge and surface-mine laws become more stringent, we can expect the demand to increase even more. The energy crisis will result in a significant increase in coal mining, thus placing further demands on the supply.

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SELECTION OF LIMESTONES AS NEUTRALIZING AGENTS FOR COAL-MINE WATER

by

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ABSTRACT

Limestone neutralization of acid mine drainage has been proposed and examined as a method of treatment. However, limestones differ greatly in composition and structure. The reactivity of 14 selected limestones was studied, both by chemical and physical properties and by relative effectiveness in neutralizing synthetic and actual mine waters, and several guidelines for the choice of limestones are given. The particle size should be at least as small as 74 microns and preferably smaller. The most effective limestones are most nearly pure calcium carbonate. Stones which have a relatively low calcium content but which contain calcite and have a large surface area are also effective neutralizers. Magnesite and dolomitic limestones are much less reactive. Disadvantages in using even the most reactive limestones for neutralization are indicated.

INTRODUCTION

For the past several years, Bituminous Coal Research, Inc. (BCR), has been active in the field of mine drainage control by sponsoring, with others, a number of research projects in this area (Bituminous Coal Research, Inc., 1969, 1970, 1971a, b; Ford, 1970, 1972; Ford and Boyer, 1973; Streeter, 1970; Zawadzki and Glenn, 1968). Cosponsors of these projects have included the Appalachian Regional Commission, the United Mine Workers of America, the Commonwealth of Pennsylvania, and the Environmental Protection Agency and its predecessors. The objective of one of these projects was the development of a treatment process utilizing limestone. The overall results of this project, which has been completed, are discussed only briefly. The purpose of this paper is to describe the results of one part of the limestone treatment project, namely, the development of a method for selecting limestones as neutralizing agents for coal-mine water and for evaluating them prior to their use in a treatment operation.

The occurrence of acid drainage associated with coal mining has been well documented (Appalachian Regional Commission, 1969). Such drainage results from the dissolution of oxidation products of pyrite in normally neutral to mildly alkaline ground water. The oxidation occurs by exposure to air and water of pyritic materials associated with the coal seam. In the Appalachian region alone, more than 5,000 miles of streams are adversely affected on a continuing basis by drainage resulting from the mining of coal. The coal industry is proceeding with a vigorous abatement program by constructing water treatment plants wherever polluting waters might be discharged from active mines into open streams. At the present time, over 300 mine-water treatment plants are operating or in various stages of design and construction in the Commonwealth of Pennsylvania alone (Maneval, 1970).

In all but a few cases, neutralization with lime, calcium hydroxide, in many places in conjunction with aeration and settling ponds, is the

type of treatment used. However, the relatively high cost and, more recently, the diminishing availability of lime and the poor sludge quality, i. e., slow settling, large volumes, and low solids content, have stimulated work in the utilization of limestone (Hill and Wilmoth, 1970). The advantages which have been claimed for limestone neutralization over lime neutralization are: (a) lower costs for chemical reagent, (b) decreased hazard to the operator handling a less reactive reagent, (c) little or no harmful effect on streams and stream life from an accidental overtreatment, and (d) potential for decreased sludge volume by an increased solids content in the sludge.

The first reported application of a limestone neutralization process to coal-mine drainage was at the Calumet Mine, Westmoreland County, Pennsylvania, in 1916. The process, as described by Tracy (1920), involved mixing pow-

dered limestone with coal-mine water, thickening the precipitate by sedimentation, and drying the thickened precipitate on a steam drum. The object of the process was to prepare water for industrial purposes and iron oxide for gas purification and for use as a pigment. The process was apparently unsuccessful and was discontinued after a few years (Tracy, 1922). More recent experiences with limestone treatment of acid wastes (Gehm, 1944; Hoak and others, 1945; Jacobs, 1947) and coal-mine drainage (Anonymous, 1969; Bituminous Coal Research, Inc., 1970, 1971b; Braley, 1951; Brant and Moulton, 1960; Clifford and Sharley, 1954; Ford, 1970, 1972; Glover, 1967; Johnson, 1952; Mihok, 1970; Mihok and Chamberlain, 1968; Mihok and others, 1968; Ohyama and others, 1957; Wheatland and Borne, 1962; Zurbuch, 1963) have increased our knowledge of the process. Data available from the literature (Anonymous, 1969; Bituminous

TABLE 1. - Limestones selected for study

BCR sample number	Source	Reason for choice
1462	Basic, Inc., Gabbs, Nevada	Magnesite
1337	Mineral Pigments and Metals, Chas. Pfizer, Gibsonburg, Ohio	High Mg
1461	Basic, Inc., Gabbs, Nevada	First thought to be a magnesite, later proved to be a dolomite
1654	J. E. Baker Co., York, Pennsylvania	Poor performance in air-pollution studies at BCR
1352	H. E. Millard Lime and Stone Co., Inc., Annville, Pennsylvania	High Mg
1364	Giant Portland Cement Co., Egypt, Lehigh County, Pennsylvania	High Al
1355	Elkins Limestone, Elkins, West Virginia	High Si
1362	Nickajack Dam-Fernvale Co., Limestone TVA	High Fe
2136	Greer Limestone Co., Greer, West Virginia	Used by Bureau of Mines for coal-mine-water-neutralization studies
2135	Appalachian Stone Co., Lake Lynn Plant, Mercersburg, Pennsylvania	Used by Bureau of Mines for coal-mine-water-neutralization studies
1335	Hills Material Co., Rapid City, South Dakota	Good performance in air-pollution studies at BCR
2145	Presque Isle Corp., via Coal Research Bureau, Morgantown, West Virginia	Used in SO ₂ -removal tests at an electric power generation plant
1809	Winfield Lime and Stone Co., Inc., West Winfield, Pennsylvania	Used at Rochester and Pittsburgh Coal Co. for coal-mine-water neutralization
2177	German Valley Limestone Co., Riverton, West Virginia, via Mr. Ron Hill	Used at Norton Mine Drainage Treatment Laboratory

Coal Research, Inc., 1971b; Mihok and others, 1968; Wilmoth and Hill, 1970) indicate that limestone neutralization presently can be applied to coal-mine waters containing iron principally in the ferric, Fe^{3+} , state. Other studies (Continental Oil Company, 1971; Ford and Boyer, 1973; Mihok, 1969; Singer and Stumm, 1969; Tyco Laboratories, Inc., 1972) to understand and to enhance the oxidation to the ferric state of ferrous iron, Fe^{2+} , in coal-mine water suggest that satisfaction with this step in the treatment process has not yet been attained. This has particular implications for attempts to use limestone treatment on waters containing significant amounts of ferrous iron.

Limestones differ considerably in composition and structure. The term is a general one embracing carbonate rocks or fossils composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and alumina (Boynton, 1966). If limestones are to be used effectively as neutralizing agents for coal-mine water, it is necessary to establish criteria for evaluating stones for this purpose. This paper reports results of the evaluation of limestones in terms of the effects of chemical composition, structure, particle size, surface area, and other variables on reactivity with coal-mine water. Also presented is a method, based on the study, for selecting limestones as potential neutralizing agents for coal-mine water and for their evaluation prior to attempts to

use them in a treatment operation. Use of the method results in the selection of a relatively effective neutralizing agent in comparison with other limestones, but not necessarily an effective neutralizing agent for each treatment operation.

EXPERIMENTAL PROCEDURE

The reactivity of 14 selected limestones was evaluated by consideration of (a) their physical and chemical properties, and (b) their effectiveness in neutralizing synthetic and actual coal-mine waters.

Chemical properties of the limestones

The individual limestones are listed in table 1, together with the reasons for their selection. The chemical composition, as illustrated in table 2, was determined by conventional emission spectrographic techniques utilizing a Jarrell-Ash Model 78-000 1.5-meter Wadsworth grating spectrograph. Structure of the limestones, as shown in table 3, was determined by X-ray diffraction analysis utilizing a Picker-Nuclear powder diffraction unit.

Physical properties of the limestones

Surface area and density of the individual limestones are listed in table 4. Surface areas were measured by the standard BET (Brunauer,

TABLE 2. - Analyses of fourteen limestones selected for study

BCR sample number	Loss on ignition P(%)	Spectrochemical analyses, mineral samples, percent by weight of ignited sample (900°C)								
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
1462	48.4	3.90	1.24	1.46	80.0	11.5	0.03	<0.02	<0.1	<0.03
1337	46.5	1.40	<0.3	0.32	43.0	55.0	<0.03	0.02	<0.1	<0.03
1461	47.2	1.05	<0.3	0.30	45.0	53.0	<0.03	<0.02	<0.1	<0.03
1654	45.8	2.05	0.54	1.83	38.0	56.0	<0.03	<0.02	<0.1	<0.03
1352	42.6	8.00	2.75	1.08	30.0	56.0	0.11	0.08	0.87	<0.03
1364	30.4	28.5	10.7	3.70	4.20	46.5	0.50	0.70	2.25	0.07
1355	34.0	25.5	4.40	1.95	1.80	64.0	0.25	0.40	0.91	0.03
1362	36.1	10.6	2.17	12.8	3.80	69.0	0.12	0.03	0.20	0.37
2136	36.7	15.8	4.40	1.70	2.80	72.0	0.23	0.36	0.62	0.03
2135	34.6	19.5	6.10	2.70	2.40	66.0	0.27	0.33	1.50	0.03
1335	42.8	3.35	0.77	0.33	0.72	94.0	0.05	0.02	<0.1	<0.03
2145	41.7	5.00	1.69	0.88	1.48	90.0	0.07	0.03	<0.1	<0.03
1809	42.1	4.60	1.50	1.30	1.06	89.0	0.05	0.02	0.12	0.12
2177	42.7	1.41	0.42	<0.3	0.90	95.0	<0.03	0.02	<0.1	<0.03

TABLE 3. - X-ray analyses of fourteen limestones

BCR sample number	Compounds identified
1462	MgCO ₃ , CaMg(CO ₃) ₂
1337	CaMg(CO ₃) ₂
1461	CaMg(CO ₃) ₂
1654	CaMg(CO ₃) ₂ , CaCO ₃
1352	CaMg(CO ₃) ₂ , CaCO ₃
1364	CaCO ₃ , SiO ₂ , [6SiO ₂ ·Al ₂ O ₃ ·9MgO·7H ₂ O]
1355	CaCO ₃ , SiO ₂
1362	CaCO ₃ , SiO ₂ , α-Fe ₂ O ₃ , Ca(MgFe)(CO ₃) ₂
2136	CaCO ₃ , SiO ₂
2135	CaCO ₃ , SiO ₂
1335	CaCO ₃
2145	CaCO ₃ , SiO ₂
1809	CaCO ₃ , SiO ₂
2177	CaCO ₃

Emmett, and Teller) technique using nitrogen as the adsorbate at liquid nitrogen temperatures or by a modified BET technique utilizing a Micromeritics Model 2200 surface-area analyzer (Micromeritics Instrument Corp., n. d.). Densities were determined with a Beckman air pycnometer.

Coal-mine waters used in this study

One synthetic and two actual coal-mine waters were used in this study. The synthetic was prepared in 15-liter batches by adding reagent-grade ferrous sulfate, FeSO₄·7H₂O, to deionized water to a concentration of 220 mg/l of Fe²⁺ and then adjusting the pH to 3.0 with reagent-grade concentrated sulfuric acid.

Two actual coal-mine waters were selected for this study. The first, designated the South Greensburg discharge, is from an inactive drift mine in Westmoreland County, Pennsylvania. This discharge contained from 83 to 97 mg/l of ferrous iron and from 178 to 196 mg/l of acidity as CaCO₃, with a pH of 5.1 to 5.3 during the period of time necessary to complete the experiments.

The second, designated the Thorn Run discharge, is from a reservoir where a number of small discharges are impounded and which is also in Westmoreland County, Pennsylvania. The composition and flow rate vary widely de-

pending on surface-water runoff during periods of rainfall. This discharge contained iron mostly in the ferric state, only small amounts of ferrous iron, and from 235 to 710 mg/l of acidity as CaCO₃, with a pH of 3.1 to 3.5 during the period of time necessary to complete the experiments.

Analytical procedures

Both raw mine water and treated water samples were analyzed routinely for: (a) ferrous iron colorimetrically using o-phenanthroline, (b) cations either by emission spectrographic techniques using a Jarrell-Ash Model 78-000 1.5-meter Wadsworth grating spectrograph or by atomic absorption spectrophotometric techniques using an Instrumentation Laboratory Model IL-153 atomic absorption spectrophotometer, (c) acidity by adding hydrogen peroxide, boiling, cooling to room temperature, and titrating to pH 8.2, and (d) pH. Ferrous iron analyses were conducted on unfiltered samples. For determination of acidity, samples treated with limestone were filtered; raw coal-mine water samples were not filtered.

General procedure for neutralization reactions

Specified amounts of limestone were added to 1,500 ml of the coal-mine water to be neutral-

TABLE 4. - Density and surface area of fourteen limestones

BCR sample number	Density (g/ml)	Surface area (m ² /g)
1462	3.27	1.98**
1337	2.74	0.62*
1461	2.94	1.11**
1654	2.32	1.22*
1352	3.57	2.29**
1364	2.87	2.13*
1355	2.63	2.94**
1362	3.02	2.53**
2136	2.46	5.39*, 5.13**
2135	2.64	7.18**
1335	2.70	0.88*
2145	2.59	2.05**
1809	3.18	1.76*, 1.72**
2177	2.54	1.17**

*Standard BET.

**Modified BET.

ized. The mixture was stirred at a constant rate and aerated at a rate of 2,500 ml/min continuously for a 5-hour period. Aeration was carried out by bubbling air into the mixture through a gas diffuser at the bottom of the container. Changes in pH were recorded with time. An Orion Model 401 meter with a Sargent/Jena combination electrode was used to measure pH, and a Houston Instrument Omnigraphic T-Y recorder, Model HR-80, was employed to record changes in pH.

The amount of limestone added was twice the stoichiometric amount based on total acidity of the coal-mine water and on the assumption that the stones consisted of pure calcium carbonate. However, in one series of experiments using synthetic coal-mine water, an adjustment was made in the amount of limestone to compensate for materials in the stone other than CaCO_3 or MgCO_3 . The weight of limestone chosen was sufficient to provide twice the equivalent stoichiometric amount of pure CaCO_3 based on acidity. This amount was calculated using the formula:

Weight of limestone =

$$\frac{(2X) \times 100}{(\% \text{ CaO}) + (\% \text{ MgO}) (56.08/40.32)}$$

Where X = stoichiometric amount of pure CaCO_3 based on acidity, and % CaO and % MgO = % after ignition at 900°C.

In this same series hydrogen peroxide (0.5 ml of 30 percent solution) was added with the limestone. The amount used was approximately 1.6 times the stoichiometric requirement to oxidize the ferrous iron.

In the series of experiments designed to examine the effect of particle size of the limestones on reactivity, BCR limestone No. 1809 was crushed and sieved to obtain 10 particle-size fractions. For all other experiments reported here, and for the individual analyses and measurement of physical properties of the stones, particle-size fractions of 37 to 44 microns (325 to 400 mesh) were employed.

Neutralizing efficiency of the limestones

Evaluations of the limestones were based on consideration of the areas under the neutralization curves as compared to the areas under similar curves obtained with BCR limestones Nos. 1809, 2145, or 2177. Relative areas under the neutralization curves were measured either by (a) copying the curves on relatively constant-weight paper and cutting out the area under each curve and weighing, or (b) using a planimeter.

One study (Gill and Tao, 1968) reports the relative standard deviation for obtaining the area under a curve using a planimeter as 4.06 percent compared to 1.74 percent by the cut-and-weigh method, the latter being the more precise. The same study, though, reports the time required for the planimeter method to be half that of the cut-and-weigh method.

The limestones were also evaluated by comparing the neutralization curves with a composite neutralization curve of all results of past tests. The chemical composition, particle size, and crystalline structure of the limestones as well as the pH, ferrous iron content, and acidity of the mine water were also considered.

Effect of particle size

Ten experiments were conducted according to the general procedure. A single limestone, BCR No. 1809, was pulverized, and neutralization curves prepared by adding 10 discrete particle-size fractions of No. 1809 to synthetic coal-mine water. The amount of limestone used was twice the stoichiometric amount based on the acidity of the water.

RESULTS AND DISCUSSION

Studies utilizing synthetic coal-mine water

Because of the inherent compositional variations in actual coal-mine waters, initial limestone evaluation studies were conducted using synthetic coal-mine water.

Effect of particle size of the limestones. — Neutralization curves were prepared, according to the general procedure, with 10 particle-size fractions of BCR limestone No. 1809 and synthetic coal-mine water. A composite of these neutralization curves is illustrated in figure 1. The particle size in microns of each fraction is listed on the appropriate curve with the corresponding mesh size shown in parentheses. The two largest size fractions, 4,760 to 9,510 microns and 2,380 to 4,760 microns, were relatively undisturbed by the mixing action and remained on the bottom of the beaker throughout the test. Size fractions between 74 and 2,380 microns effected essentially the same response—an initial increase of 2 to 3 pH units. After about 90 minutes the pH was slightly higher for the finer size fractions. As indicated in figure 1, the response from size fractions below 74 microns was significantly different. An immediate increase to about pH 6 was observed,

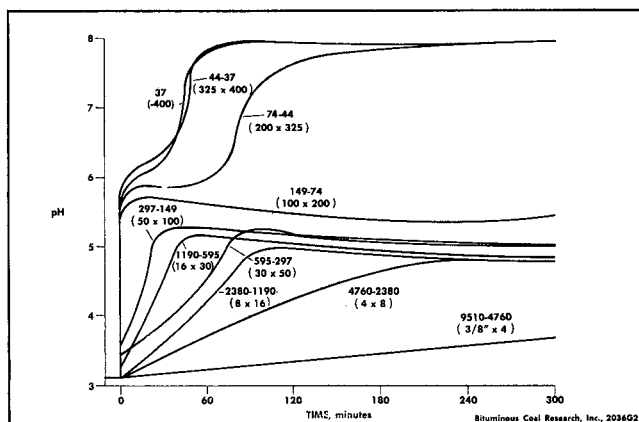


FIGURE 1. - Effects of particle size of limestone No. 1809 on neutralization of synthetic coal-mine water. Particle size in microns is shown for each curve; mesh size is shown in parentheses.

followed by a further less rapid increase to approximately pH 8. This series of experiments led to the choice of the 37- to 44-micron (325- to 400-mesh) fractions for all further experiments discussed in this paper.

Effect of calcium, magnesium, surface area, and density of the limestones. — The curve in figure 2 is the neutralization curve produced by the addition of finely divided limestone No. 1809 to synthetic coal-mine water. At point A most

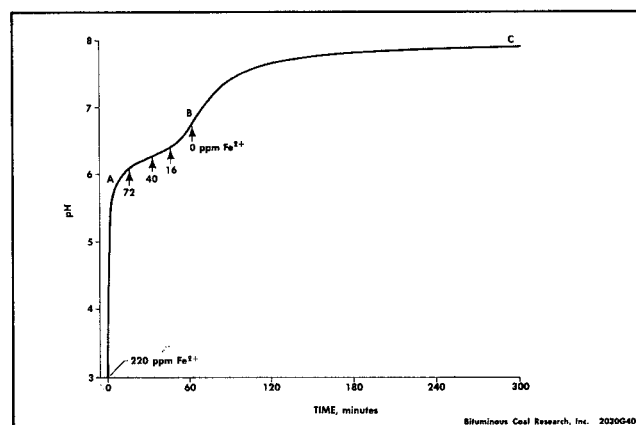


FIGURE 2. - Effect of limestone No. 1809 on synthetic coal-mine water. At point A most of the free acid had been neutralized; from A to B most of the ferrous iron was oxidized; from B to C the last traces of ferrous iron were oxidized.

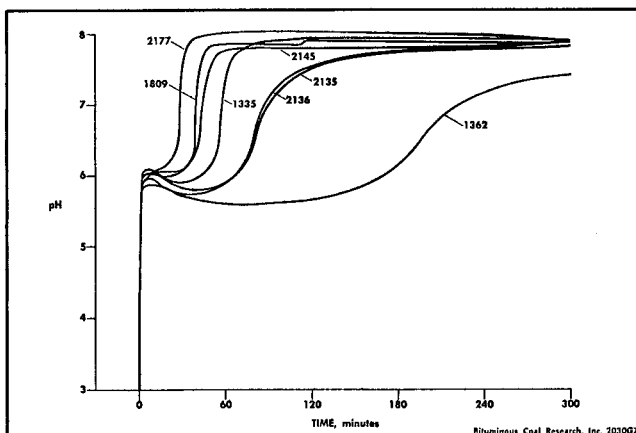


FIGURE 3. - Effects of Group A limestones on synthetic coal-mine water. Stones of this group effected a greater change in pH than did stones of Group B.

of the free acid had been neutralized. The portion of the curve from A to B represents the oxidation of most of the ferrous iron. The portion from B to C represents the increase in pH as the last traces of ferrous iron have been oxidized, and the free acid generated by this oxidation has been neutralized.

Each of the other stones was tested in a similar manner. The neutralization curves are presented in figures 3 and 4. The limestones have been grouped in these figures according to the overall appearance of the curves rather than pH attained at one point in time or some other arbitrary

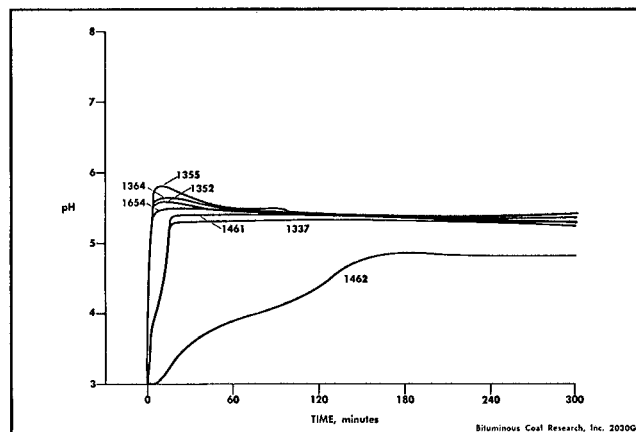


FIGURE 4. - Effects of Group B limestones on synthetic coal-mine water. Stones of this group effected less change in pH than did stones of Group A.

trarily chosen standard. Group A limestones effected a greater change in pH than those of Group B.

An interesting trend is shown in table 5. The pH attained one hour after the addition of limestone and the start of aeration, before equilibrium (complete ferrous iron oxidation) had been attained, was arbitrarily chosen as an indication of neutralizing efficiency. From these data, neutralizing efficiency of a stone generally increased with higher percentages of calcium oxide, CaO, and lower percentages of magnesium oxide, MgO, present in the limestone. The relationship holds slightly better for MgO than it does for CaO. The data, however, show calcites, CaCO_3 , to be more effective than dolomites, $\text{CaMg}(\text{CO}_3)_2$, or magnesites, MgCO_3 .

Efficiency, for the purposes of this paper, is directly related to the area under the individual neutralization curves; the greater the change in pH as a result of limestone addition, the greater the area. Reactivity in this context is considered synonymous with efficiency.

A mathematical expression relating efficiency and some property or properties of a given limestone would be most useful as a means of evaluating limestones. Some of the empirical relationships considered in evaluating these data are listed in table 6. The order in which the limestones were arranged in this table was

TABLE 5. - Effect of calcium and magnesium content of limestone on pH, one hour after addition of limestone and air

BCR sample number	pH attained one hour after addition of limestone and air	Spectrochemical analyses, percent of ignited (900°C) sample	
		CaO	MgO
1462	3.92	11.5	80.0
1337	5.30	55.0	43.0
1461	5.38	53.0	45.0
1654	5.47	56.0	38.0
1352	5.48	56.0	30.0
1364	5.51	46.5	4.20
1355	5.52	64.0	1.80
1362	5.58	69.0	3.80
2136	5.86	72.0	2.80
2135	5.89	66.0	2.40
1335	7.37	94.0	0.72
2145	7.77	90.0	1.48
1809	7.85	89.0	1.06
2177	7.98	95.0	0.90

TABLE 6. - Empirical relationships considered in evaluating limestones

BCR sample number	CaO x SA*	CaO x SA/MgO	CaO + SA	CaO + (SA) ²	CaO + (SA x D**)
1462	22.8	0.3	13.5	15.4	18.0
1337	34.1	0.8	55.6	55.4	56.7
1461	58.8	1.3	54.1	54.2	56.3
1654	68.3	1.8	57.2	57.5	58.8
1352	128.2	4.3	58.3	61.2	64.2
1364	99.0	23.6	48.6	51.0	52.6
1355	188.2	104.6	66.9	72.6	71.7
1362	174.6	45.9	71.5	75.4	76.6
2136	378.7	135.2	77.3	99.7	84.9
2135	473.9	197.4	73.2	117.6	85.0
1335	82.7	114.9	94.9	94.8	96.4
2145	184.5	124.7	92.0	94.2	95.3
1809	154.9	146.1	90.7	92.0	94.5
2177	111.2	123.6	96.2	96.4	98.0

*Surface area.

**Density.

that suggested by data in table 5. The best relationship selected for evaluating limestones was $[\text{CaO} + (\text{surface area} \times \text{density})]$.

The data corresponding to the neutralization curves in figures 3 and 4 are listed in table 7 in order of increasing efficiency, based on the area under the neutralization curves relative to the area under the curve for limestone No. 2177, the most efficient one in this series. The relationship $[\text{CaO} + (\text{SA} \times \text{D})]$ is presented in the last column. Generally, there was a correlation between this relationship and the areas under the neutralization curves. Also presented in this table are the levels of pH attained 30, 60, and 300 minutes after the addition of limestone and start of aeration.

Consideration of the results shown by figures 3 and 4 and the data from tables 2, 3, and 4 revealed that magnesite (No. 1462) is the least effective neutralizing agent, followed closely by dolomitic limestone (Nos. 1337, 1461, 1654, and 1352). Samples Nos. 1654 and 1352 contained some calcite in addition to dolomite, and therefore ranked higher than Nos. 1337 and 1461, which contained no calcite.

Of somewhat intermediate reactivity were Nos. 1364, 1355, and 1362, calcites containing large percentages of impurities. Limestones Nos. 1364 and 1355 contained greater than 25 percent quartz, SiO_2 .

Limestone No. 1362 also contained quartz (approximately 10 percent) as well as compounds containing Fe, Ca, and Mg. However, since this stone contained a higher percentage of CaO than either No. 1364 or No. 1355, its reactivity was higher than that of No. 1364 or No. 1355.

In spite of the presence of relatively large amounts of quartz (greater than 15 percent) and relatively low percentages of CaO (approximately 70 percent), limestones Nos. 2135 and 2136 were effective apparently because of high surface area, 7.18 and 5.26 m^2/g , respectively, compared to the average, 2.36 m^2/g , of the 14 limestones. Conversely, No. 1335, almost a pure calcite (94.0 percent CaO) ranked slightly below No. 2145 (90.0 percent CaO) and No. 1809 (89.0 percent CaO). The surface area, 0.88 m^2/g , of No. 1335 was one of the lowest in this series.

Limestones Nos. 2145 and 1809 were almost identical in reactivity, composition, and structure. The most effective limestone in this series was No. 2177, essentially a pure calcite. Even the silica content of this limestone was too low to be detected by X-ray diffraction analysis.

Effect of impurities in the limestones. — In one series of experiments, the amount of limestone added was adjusted to compensate for components other than CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, or MgCO_3 . The 14 stones were tested as before. The data from the neutralization curves are shown in table

TABLE 7. - Efficiency of limestones with synthetic coal-mine water

BCR sample number	Relative area under curve	pH after			CaO + (SA x D)*
		30 min	60 min	300 min	
1462	30	3.6	3.9	4.9	18.0
1337	46	5.3	5.3	5.3	56.7
1461	48	5.4	5.4	5.3	56.3
1654	49	5.5	5.5	5.3	58.8
1352	49	5.5	5.5	5.4	64.2
1364	50	5.6	5.5	5.4	52.6
1355	52	5.6	5.5	5.5	71.7
1362	69	5.7	5.6	7.4	76.6
2136	87	5.7	5.9	7.8	84.9
2135	87	5.8	5.9	7.8	85.0
1335	94	5.9	7.4	7.9	96.4
2145	95	6.0	7.8	7.9	95.3
1809	96	6.1	7.8	7.9	94.5
2177	100	7.6	8.0	8.0	98.0

*Surface area x density.

TABLE 8. - Effect of impurities on limestones

BCR sample number	Relative area under curve	Factor* used in adjusting amount of limestone	CaO + (SA x D)**
1462	19	0.81	18.0
1654	32	0.95	58.8
1337	33	0.89	56.7
1461	40	0.79	56.3
1352	78	1.05	64.2
1364	87	1.64	52.6
1355	89	1.64	71.7
1335	91	1.08	96.4
1362	94	1.73	76.6
2135	96	1.44	85.0
2136	97	1.37	84.9
1809	98	1.15	94.5
2177	99	1.04	98.0
2145	100	1.09	95.3

*Factor = $\frac{\text{Wt. of limestone needed, compensating for impurities}}{\text{Wt. of limestone, assuming pure CaCO}_3}$

**Surface area x density.

8. The limestones are arranged, based on the areas under the neutralization curves, in order of increasing efficiency. Few significant differences from the results listed in table 7 were noted. Increases in the amounts of limestones which contained calcite generally resulted in increases in the areas under the curves. Magnesite and dolomites showed little or no change in pH response.

Studies utilizing actual coal-mine water

The 14 limestones, particle-size range 37 to 44 microns, were tested with both the South Greensburg and Thorn Run coal-mine discharges in a manner identical to that used for the synthetic coal-mine water. Each experiment was conducted on the same day that a sample of the coal-mine water was obtained. The results of these neutralization experiments are presented in table 9.

The South Greensburg water, which contains iron principally in the ferrous state, more closely approximates the synthetic coal-mine water than does the Thorn Run discharge, which contains iron principally in the ferric state. The overall shapes of the neutralization curves from the South Greensburg tests resemble the curves from the tests with the synthetic water, as illustrated in figure 5 by an example of one

TABLE 9. - Efficiency of limestones with South Greensburg and Thorn Run coal-mine discharges

BCR sample number	Relative area under curve	
	South Greensburg discharge	Thorn Run discharge
1462	16	14*
1461	19	24
1337	25	38
1654	26	47*
1352	36	47*
1364	44	76*
1355	55	58
1362	62	94*
2135	70	100*
1335	78	91
2136	79	92
1809	84	93
2145	97	97*
2177	100	98

*Substantially greater amount of limestone used than twice the stoichiometric amount based on acidity.

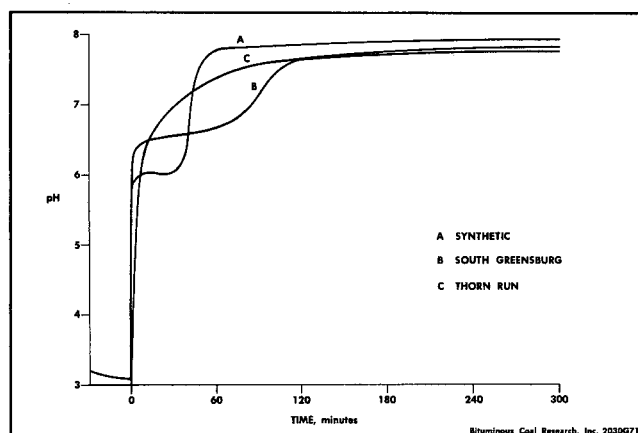


FIGURE 5. - Effect of limestone No. 2145 on three coal-mine waters.

curve from each of these tests. Also included in this figure is one of the curves from the tests with the Thorn Run discharge. The absence of ferrous iron in the Thorn Run discharge is demonstrated by the absence of the inflections typical in previous curves with the synthetic and South Greensburg waters, where ferrous iron was present.

Heavy rains during the periods over which these experiments were conducted resulted in

TABLE 10. - Relative effectiveness of limestones with synthetic and actual coal-mine water systems

Synthetic coal-mine water	South Greensburg discharge	Thorn Run discharge
1462*	1462	1462
1337	1461	1461
1461	1337	1337
1654	1654	1654
1352	1352	1352
1364	1364	1355
1355	1355	1364
1362	1362	1335
2136	2135	2136
2135	1335	1809
1335	2136	1362
2145	1809	2145
1809	2145	2177
2177	2177	2135

*BCR sample number.

changes in composition in this water from day to day. The acidity of a sample on any particular day was sometimes twice that of a sample taken the following day. The quantity of limestone required on a given day was determined from the acidity of the previous day's sample, thereby complicating the determination of the limestone requirement, as indicated by the data in table 9. As described earlier, Thorn Run is essentially a reservoir for a number of small discharges; therefore, the water from this site is more affected by weather conditions than is the water from the South Greensburg site, where sampling is done at the point of discharge.

In table 10, the limestones are listed in order of increasing effectiveness, based on the area under the neutralization curves. The relative effectiveness of the 14 limestones with the South Greensburg and with the Thorn Run discharges is compared to the relative effectiveness with synthetic coal-mine water. Agreement between results of tests with the synthetic coal-mine water and those with the actual coal-mine waters is good, as reflected by the similar rankings of the limestones in table 10. Test results with the synthetic coal-mine water are in better agreement with those obtained using the South Greensburg discharge than with those obtained using the Thorn Run discharge. The difficulties as a result of the compositional variability of the Thorn Run discharge, the greater similarity between the synthetic and the South Greensburg water due to the predominance of ferrous iron in both, and the absence of appreciable quantities of ferrous iron in the Thorn Run discharge have already been mentioned.

An attempt was made to simplify this test for evaluating limestones by using only dilute sulfuric acid as the test water. Some of the differences between reactivity of the 14 limestones were amplified, but overall there was poor agreement with the results of other tests, apparently due to the presence of inert materials, particularly silica, in the stones. The test had in fact been simplified by the use of dilute sulfuric acid, but the results seemed less meaningful in relation to the neutralization of coal-mine water.

Summary

To summarize the evaluation of the 14 limestones, a series of curves combining all results of the neutralization experiments is presented in figure 6. The curves of those limestones which were effective in neutralizing coal-mine water, namely Nos. 1335, 1809, 2135, 2136, 2145, and 2177, are contained within area A on this figure. The curves of those stones which were judged to

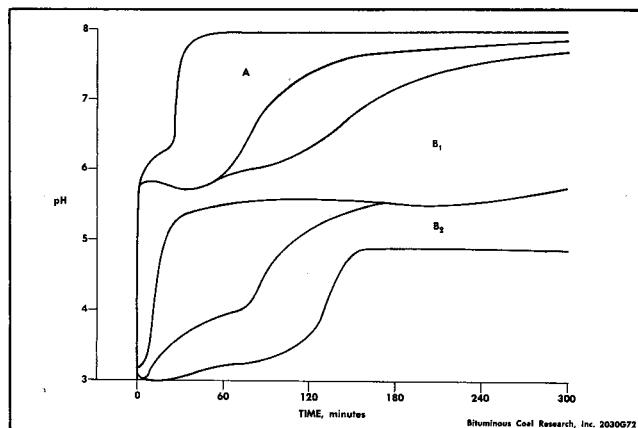


FIGURE 6. - Areas encompassing model curves for judging effectiveness of limestones (based on preliminary neutralization tests). Area A, limestones effective in neutralizing coal-mine waters; areas B₁ and B₂, limestones ineffective in neutralizing coal-mine waters.

be ineffective, namely Nos. 1337, 1352, 1355, 1362, 1364, 1461, 1462, and 1654, are contained within areas B₁ or B₂.

Similar studies were conducted with 12 more limestones which were procured in the finely divided state; for example, limestones commercially available as rock-dusting material, for agricultural use, etc. These samples were analyzed as received for particle size and chemical composition, used in the tests, pulverized further, and used again in the tests. The results of these tests reenforced the conclusions drawn earlier. Particle size, again, was determined to be a most significant factor.

Sufficient data should be available from the neutralization experiments described here to select the best of the limestones for neutralization, based only on the chemical and physical properties of the stones. If such data are not available or if further evaluation of a selected stone is desired, then a test method to evaluate a particular limestone should be available.

Recommended test method

The following test is recommended to evaluate limestones as potential neutralizing agents for coal-mine water:

Finely divided (37 to 44 microns, 325 to 400 mesh) limestone should be added and air introduced to a solution of synthetic coal-mine water at pH 3.0 and containing 220 mg/l of Fe²⁺ added as ferrous sulfate; this solution should be stirred and aerated continuously for a 5-hour period and

the changes in pH recorded with time. The amount of limestone added should be twice the stoichiometric amount based on the acidity of the synthetic coal-mine water and based on the assumption that the stone consists of pure CaCO₃. Air should be bubbled into the solution through a gas diffuser at the bottom of the container. The aeration should be maintained throughout the reaction at a rate of 2,500 ml/min.

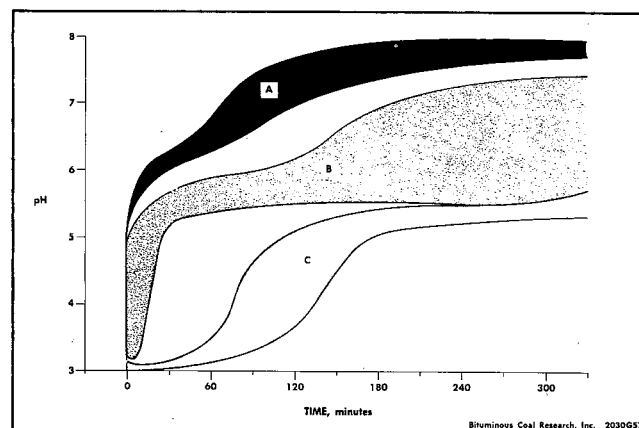


FIGURE 7. - Areas encompassing model curves for judging effectiveness of limestones (composite based on all past tests). Area A, limestones effective in neutralizing coal-mine waters; areas B and C, limestones ineffective in neutralizing coal-mine waters.

A composite curve including results from all past tests should be used to judge the results of this test. The curve from an effective limestone would be located in area A of figure 7; curves from ineffective limestones would be located in areas B or C. Finally, the test should be repeated with the coal-mine water to be treated and with the selected limestone.

Use of limestone in a treatment process

As a result of additional studies at BCR on treatment of acid mine drainage with limestone, it has been concluded that limestone treatment has only limited application for treatment of such water. When acid mine water contains iron principally in the ferric state, it might be possible to use limestone as the neutralizing agent if the stone meets the criteria for an effective neutralizing agent as described in this paper.

The successful application of limestone treatment to mine waters containing significant quan-

tities of ferrous iron hinges on an additional means of enhancing the rate of iron oxidation during treatment. Limestone and aeration alone are not adequate to accomplish this oxidation in a reasonable time period during neutralization. Thus far, studies have not been successful in finding an economical practical means of oxidizing ferrous iron for use with limestone neutralization.

CONCLUSIONS

A method has been developed for evaluating limestones as neutralizing agents for coal-mine

water. Use of this method has established the following criteria to aid a potential user in the selection of a particular limestone:

For use in a treatment operation a particle size of 74 microns (200 mesh) and preferably smaller is one of the most important criteria. The most effective limestones are those approaching pure calcium carbonate in composition. Those stones which have a relatively low calcium content, but which contain calcite and have a high surface area, are equally effective neutralizing agents. Magnesites are the least effective neutralizing agents, followed closely by dolomitic limestones.

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LIMESTONE FOR CONTROLLING ACID MINE DRAINAGE AND FOR TREATMENT OF ACID MINE WATER

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ABSTRACT

Limestone can be used effectively in treating acid mine water. Aside from a lower cost than for other treatment agents, limestone has the advantages of easy storage and effectiveness even when impure and in slack sizes. Limestone incorporated into waste piles in layers or as riprap can inhibit acid formation; limestone rubble packed in a mine entry offers promise in formation of a low-cost autogenous resilient seal.

INTRODUCTION

Pollution is a nuisance. The most effective method of coping with a nuisance is to get rid of it. Treatment of acid mine water merely minimizes the nuisance; it by no means eliminates the nuisance and commonly creates more nuisances—like sludge ponds and piles of unsightly goo. It is my thesis that industrial minerals—and limestone is no exception—will be used freely only when the benefits are permanent, or at least long lasting.

The mine operator, as a part of the business sector, finds himself investing more and more manpower and capital for plant facilities, real estate, and reagents. I know of no industrialist who does this ungrudgingly—coal mine operators are not unique in this respect. Acid mine water and the consequences of treatment are found to be a nuisance by still another element of the business sector: those businesses that require land and low-cost water supply that cannot be readily acquired because land is occupied by sludge ponds or piles of saturated gelatinous precipitate.

The public sector likewise finds acid mine water and the results of treatment a nuisance. As property owners, vacationers, sportsmen, or naturalists, we all feel resentment over the ravaged landscape. The governmental sector

finds itself assailed by citizens who want the scarred landscape and polluted waters of the nation restored to some useful form and by businessmen who feel that they are unfairly subjected to unanticipated operating costs.

No one wins at this kind of game. It is necessary for those of us who can assume some responsibility for seeking practical solutions to begin now to reduce the problem to manageable proportions, while seeking more permanent long-term solutions. This means that we must somehow arrest the formation of acid water. Unless this is accomplished, an ever-increasing share of our resources will be devoted to maintaining a less than satisfactory ecological equilibrium.

INHIBITION OF ACID FORMATION

Acid water forms freely whenever pyrite is exposed to air and water. Good management in mine-refuse disposal and judicious use of limestone mixed with the acid-forming material can prevent acid formation. This fact is proven easily by simply mixing a range of concentrations of finely pulverized limestone, such as mine-rock dust or agricultural lime, with pyritiferous rock. These mixtures can be alternately water saturated and dried and compared with a standard

or blank that is untreated. A remarkably small amount of limestone is needed to inhibit acid formation, far less than that required to neutralize the acid that would have formed if all the pyrite were oxidized.

The reason that limestone inhibits acid formation is no different than the reason that any other base will. The oxidation of pyrite ultimately yields ferric sulfate, which in turn increases the rate of oxidation of the remaining pyrite. Once this process starts, the acid already formed must be neutralized before any excess of alkaline agent becomes available to act as an inhibitor. Limestone is the only relatively insoluble material that can be practically and effectively used for this purpose. Even if cost was not a consideration, such other alkaline agents as lime, sodium carbonate, sodium hydroxide, potassium hydroxide, and ammonium hydroxide are too soluble to be used as inhibitors.

Limestone has other properties and characteristics which make it useful and desirable: low cost, ready availability, effectiveness regardless of impurities or diluents, noncritical concentrations, easy storage, and no toxic effects. In fact, in very fine suspensions it is used as an antacid for stomach upset.

An effective, albeit highly specialized, example of the use of limestone to inhibit acid formation resulted from an inquiry made to the Bureau for recommendations on how to build a plant for treating acid water formed when Pennsylvanian coking coal, stockpiled in Japan, yielded a stream of red water, which the local fishermen claimed was causing fishkills in Japanese rivers. Rather than recommending a design for the construction of an acid drainage treatment plant in Japan, we recommended that limestone be used to inhibit the formation of acid. Some rather simple tests were suggested and performed. The result was that 320 pounds of rock dust per hour are added to the 140-ton-per-hour coal stream as it is loaded. This is only 2.3 pounds of limestone dust per ton of coal, scarcely more than 0.1 percent. Because the coal is used for metallurgical coke manufacture, the slight addition of lime has no deleterious effect. This practice has been in operation for more than a year, and no acid water has been found from the stockpiles in Japan even during the heavy-rain season in June and July and during several hurricanes.

This demonstration should stimulate the use of limestone to inhibit formation of acid from any kind of potential acid-forming refuse pile. Coal-mine and metal-mine refuse piles can be limestone dusted and compacted as they are

being formed. The compaction to reduce the flow of water through the pile and the limestone dusting to reduce the amount of acid formed can do much to reduce the effort expended to meet environmental standards.

LIMESTONE USE ON EXISTING ACID-FORMING REFUSE PILES

All of the acid already formed must be neutralized before inhibition can become effective. The acid from large and uncompacted refuse piles, especially those long neglected, is extremely difficult to control. A treatment plant designed and built to neutralize the acid so formed must be operated until all the acid-forming material in the refuse pile has been oxidized. Experience has shown that a refuse pile can produce an enormous quantity of acid over a very long period of time; thus such approaches have not been very successful.

A better approach is based upon recognition of the fact that acid salts already formed in refuse heaps must be allowed to leach naturally while beginning inhibition. This can be accomplished practically by packing the perimeter of the base of the refuse pile with crushed limestone so that the acid-water effluent is neutralized as it seeps from the pile; simultaneously the remaining surface of the pile must be covered with limestone rubble. Certainly this would require large tonnages of limestone, some construction, and earth moving, but once this was accomplished the job would be done—and done permanently. But remember, only enough limestone to neutralize existing acid is needed, as the limestone veneer inhibits the formation of more acid.

SELF-SEALING LIMESTONE PLUGS FOR MINE OPENINGS

When an above-drainage underground mine has been abandoned, the probability that it will produce an acid mine water pollutant is high. Many of these abandoned mines present particularly difficult problems because they are relatively inaccessible where there has been second growth of trees and shrubs or where the sites have become involved in real estate developments. If the acid-producing mine is sealed with masonry stoppings, extensive construction, involving clearing, supporting entries, notching ribs, bracing floor and roof, installing reinforcing rods, building forms, and pouring concrete, is required. These seals have proven to have lim-

ited utility and to require regular inspection and maintenance because they tend to crack as adjacent mine pillars slough and the load on the seal increases. The vast number of such abandoned mine openings that are currently producing acid water presents an enormous problem and an extremely expensive undertaking if masonry seals are to be used. The use of limestone plugs is an attractive alternative.

Limestone has some real advantages for sealing mine openings. Limestone is cheap, it can contain a high percentage of impurities and still be effective, the size consist is not critical, it requires no special handling facilities, and it can be stored as received for a long time without losing effectiveness.

And there are yet other reasons why limestone should be used. It is self-sealing when in contact with flowing acid mine water. A study conducted for the Environmental Protection Agency showed limestone to be suitable for such a purpose. Unfortunately, these were small-scale laboratory tests, which could not be used to extrapolate the potential benefits to be derived from full-scale demonstrations. I have observed coarse-limestone-lined ponds, where treated acid water was being aerated, that were solidified by the precipitated gypsum and iron oxide hydrates. Steel pipes carrying treated water soon become clogged with similar precipitates.

A limestone plug emplaced in an abandoned mine opening by a remotely operated pneumatic or mechanical stower could create a porous plug that would quickly seal itself. The laboratory tests referred to were conducted in 6-inch-square 6-foot-long smooth-walled ducts. Full-scale tests should be conducted in openings approximately 6 feet high and 10 feet wide and with limestone rubble emplaced to a depth of 50 feet or more—some 60 to 70 tons of limestone. A plug so emplaced would very quickly reduce the flow to a trickle.

Perhaps the greatest advantage of such a plug is the fact that it is resilient. The effectiveness of plugs in abandoned mines will be greatly enhanced if required inspection and maintenance can be eliminated or reduced substantially. Because limestone rubble admixed with impurities and cemented or filled with gypsum, iron oxide hydrates, and other precipitates has a self-sealing capability, a plug of this composition would not fail catastrophically and would continually repair itself by mechanically trapping suspended sediments and by crystallization from solution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). As with any seal, there is the potential hazard

of building up a large hydraulic head behind the limestone plug where the coalbed pitches up. For example, a 100-foot head of water exerts a pressure of approximately 50 psi at the face of a plug or seal. A well-packed limestone plug, especially under the high confining pressure of the overburden, will strongly resist a pushing force, even though it may fracture. It is estimated that an emplaced limestone plug 50 feet deep will resist a pushing force of 30 psi (60-foot head). Where high hydraulic pressures are anticipated provisions for pressure relief should be made.

One advantage to sealing mines where the coalbed is flat or pitches down is that the mine floods and the oxygen in the mine water soon becomes depleted, acid formation ceases, the mine water becomes stagnant, and phreatic water that normally would enter the mine opening gradually seeps out at the periphery of the coalbed as natural springs. This is infinitely more desirable than the flow with yellow-red residues commonly seen coming from mine openings and so emblematic of past neglect.

LIMESTONE FOR ACID MINE WATER TREATMENT

The use of limestone for treating acid mine waters could provide a perpetual market for the limestone industry if treatment alone were considered the optimum means of dealing with the problem; where all else that is practical has been done and a flow of acid water persists, this residual source should be treated with a limestone slurry. The scientific and engineering basis for this has been amply demonstrated and supported. To the best of my knowledge, there is not yet a single mine drainage treatment plant operating that uses limestone slurry as a neutralizing agent. For those who may wish to try it, I offer but one admonition—the limestone will not be efficient for neutralization unless it is ground to a median size no larger than 10 microns. Rock dust used to control coal-dust explosions in mines or agricultural limestone powder will not be efficient—they are both too coarse. The fine limestone slurry produced in the Bureau of Mines tests not only was effective in neutralizing the acid but it also yielded a much lower volume of sludge than did slaked-lime treatment.

The low cost of limestone, even after milling to a less-than-10-micron median size, along with all the other advantages of nontoxicity, easy handling, and low volume of sludge, would appear to preclude the use of any other treatment agent. But such has not been the case.

MARKET POTENTIAL FOR LIMESTONE FOR ACID MINE-WATER CONTROL

The market for limestone should be long lasting, reaching a peak in the near future as reclamation of mined land becomes a matter of major public concern and action, and subsequently declining slowly.

Probably the greatest demand will be for impure run-of-mine or waste sizes because of their low cost and adequacy for surface treatment of waste piles or for mine sealing. The

many hundreds of mine openings that must be sealed, requiring perhaps 60 to 70 tons of limestone each, and the hundreds of waste heaps, requiring perhaps 350 tons of limestone per acre of exposed surface, in total will require on the order of 1 to 10 million tons of limestone. This amount is insignificant, however, in view of the almost 50 million tons produced annually in Ohio alone. But the benefits to be derived from the usage will be permanent, economical, and environmentally enriching.

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ROCK TYPES AND LABORATORY ANALYSES AS A BASIS FOR MANAGING MINESOILS¹

by

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ABSTRACT

Mining-related earthy bodies in contact with the atmosphere are now counted, generally, as minesoils. Because soils within this broad category are extremely young the influence of parent material is stronger than in older soils, where climate, organisms, and topography have had time to interact with near-surface rocks to form more distinctly differentiated profiles. Understanding of minesoil properties and processes is aided by definitions of rock types in terms of chemical, physical, and mineralogical characteristics that are, with some degree of consistency, translatable into soils. Geological correlations based on age or sedimentary sequences are helpful if they assure details of mineralogy and lithology, but our pedologic objectives demand that any conflicts involving rock types must be resolved in favor of distinctions having strongest implications for soil properties after mining. Chemically this approach emphasizes accounting of potential acid-base status, plant nutrient availability by adapted and calibrated extraction procedures, and absence of biotoxins. Physically it anticipates particle sizes, shapes, and arrangements in readily pervious soil profiles that will favor plant growth with desired levels of moisture and oxygen. Concurrently we are considering soil property suitability for uses other than growth of plants. Above all we need to be able to predict pedogenic processes in the particular environment, including rate as well as direction of chemical and physical change.

INTRODUCTION

Concepts of "soil" differ among disciplines and in response to needs of use and management. Within the U. S. Department of Agriculture and cooperating state Agricultural Experi-

ment Stations that accept the system of soil classification embodied in the American comprehensive system, Soil Taxonomy (National Cooperative Soil Survey, 1970), concepts have evolved to the point that soil is now defined as follows: "The collection of natural bodies on the earth's surface, in places modified or even made by man of earthy materials containing living matter and supporting or capable of supporting plants out of doors."

There is no doubt that this definition includes bodies of fragmented earth materials formed by mining. Moreover, the system in Soil Taxonomy, by design, is broad in scope and flexible enough

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to accommodate in useful categories all kinds of earthy bodies defined. Having accepted this viewpoint, we prefer to neglect the term "mine spoils" and to accept "minesoils," instead, as the broad blanket term for mining-related bodies on the earth's surface. This term is appropriate for classification, scientific study, and management within classes listed in Soil Taxonomy.

Since the nature of parent material has a marked effect on properties of minesoils, it is useful to categorize coal overburden in rock groups that have predictable influences on the kind of soil that develops. General discussions of the effect of rock types as soil parent material can be found in Buol and others (1973), Ollier (1969), and others. In this connection, a major problem has been how to use rock-type terminology in such a way that we convey intended meanings among our local groups as well as to distant neighborhoods and other disciplines. Examples of usages that apply to this paper are as follows:

Sandstones

By our definition sandstones contain more than 50 percent sand-size (less than 2 mm and greater than 0.05 mm in diameter) particles, which commonly are predominantly quartz and may be cemented with silica, iron oxide, carbonates, or clays. Our use of the 0.05-mm particle-size boundary has no justification except conformity with U. S. D. A. Soil Survey standards. In practice we would not claim sufficient skill to distinguish between 0.05-mm and 0.062-mm diameters except by laboratory methods. Qualitative modifiers such as calcareous, argillaceous, and pyritic, for example, are used on judgment basis when they seem to add useful information. Soils formed from sandstones tend to have coarse textures and to be highly pervious. In the Appalachian region such soils generally are lower in base status, plant nutrient reserves, and pH than soils derived from mudrocks, but there are striking exceptions that may not be anticipated. Proportions and porosity of coarse fragments are important variables that depend on strength of cementation and mineralogy.

Shales

Shales are thinly laminated (fissile) mudrocks (or lutites) composed of silt- and clay-size sedimentary particles (less than 0.05 mm in diameter). The coarser size types are com-

monly called siltstone, but we find this distinction difficult to standardize among observers. The mineral composition of shales is not considered diagnostic, but in coal measures sediments of this region, micaceous layer silicates with 10Å planar spacings commonly dominate the less-than-2-micron fraction, whereas quartz is likely to be quantitatively dominant in coarser (silt-size) fractions. From the soils viewpoint other mineral or amorphous constituents may be more reactive, physically or chemically, and hence more important to minesoils. Among such constituents are carbonates, pyrites, allophanes, feldspars, chlorite, and impure coal. In addition there may be distinctly different mineral species blanketed under the "micas" identified by the fixed 10Å planar spacing.

Mudstones

Mudstones are composed of the same general particle sizes as shales, but are of a more massive form and tend to fracture into blocky units with flat or conchoidal faces; they lack the fissility of shales. Various mudstones are locally called "soapstone," "fire clay," "underclay," and "flint clay" (conchoidal fractures), but we have not been able to achieve consistent usage of these terms among our soils, geologic, and conservation coworkers, especially when the fragmented rocks are seen in minesoils rather than in the geologic section. In some cases high-alumina clays are abundant, and resulting soils should have relatively high anion-exchange but low cation-exchange capacity, even though clay percentages are high. Minesoil management difficulties may occur with either silty or clayey textures because of weak structure. Plant nutrient reserves may be adequate, and carbonates may be present at any level below that of a recognized limestone or dolomite.

Carboliths

We have coined the name carbolith to encompass in minesoils the so-called black shales associated with coals, as well as impure waste coal, bone coal, and other high-carbon shales. This category of rock has a Munsell streak or powder value of 3 or lower and contains at least 25 percent carbonaceous matter oxidizable at 400°C. Many carboliths contain more pyrite than associated coals. These rocks may contain carbonates or simple or complex sulfate salts, as well as the wide range of minerals found in common shales or mudstones.

Limestones and dolomites

Definitions of limestones and dolomites based on minimum percentages of carbonates have not been satisfactory in our minesoil studies, which involved field logging of rock exposures and profile descriptions of minesoils. For these purposes we have chosen to require that limestone be cemented well enough to exhibit hardness greater than 2.5 (Mohs' scale), as well as an unmistakable effervescence of the intact or powdered rock in 10 percent hydrochloric acid. This definition leaves all of the soft impure carbonate-rich units under the general classification of calcareous mudrocks. If fissile such rocks are calcareous shales; if nonfissile they are calcareous mudstones. Only the well-cemented carbonate rocks that are judged likely to remain as coarse fragments are called limestones or dolomites. Siderite-rich rock layers and nodules should be included with cemented limestones because they will persist as coarse fragments. Limestone impurities may include many minerals, but these are relatively unimportant to minesoils for the foreseeable future because they are sealed within resistant coarse fragments of carbonates. Calcareous mudstones, on the other hand, are expected to contribute many soil fines; the chemical behavior of these rocks will require analyses for carbonates, calcium, magnesium, phosphorus, and other elements to clarify processes and properties in minesoils.

CHEMICAL ANALYSES

Laboratory analyses have long been recognized as essential for most efficient use of agricultural lands. Equivalent knowledge of the concentration and rate of release of available plant nutrients is necessary for the most economical management of minesoils, whether for legal reclamation success or subsequent intensive land use. It is not always appreciated that chemical extraction procedures must be appropriate for the particular minesoil if consistently useful results are to be obtained.

In materials where there is a history of high acidity resulting from oxidation of sulfides, or where the development of such mineral acidity is suspected, analyses for pyritic sulfur and determination of total reactive base content by a neutralization procedure are recommended (Grube and others, 1973). These two measurements provide a basis for estimating the potential of the minesoil for: (1) generating extreme acidity over a long period of time, (2) providing

moderate acidity that is readily neutralizable with moderate rates of agricultural limestone, or (3) remaining neutral or slightly alkaline because of natural reactive alkaline earths. The prevention of sulfate acidity by basic elements may involve inhibition of activity of ferrobacillus microbes as well as immediate formation of neutral salts.

The analysis for neutralization potential is useful also in evaluating calcareous materials that may be needed as an amendment or as topsoil for known highly acid minesoils. When the potential acidity or neutralizing capacity has been determined for a minesoil, appropriate steps can be taken to adjust the pH and neutralizers to satisfactory levels for desired plant growth, using either conventional agricultural limestone and fertilizer or locally available calcareous mudrocks. In this connection, the prime concern may be the great dependence of plant nutrient availability on the levels of soil acidity and neutralizers.

Previous work (West Virginia University, 1971) established the accuracy of the Woodruff buffer method of determining the immediate lime requirement of certain acid minesoils when compared to the direct calcium hydroxide method (Dunn, 1943). Recent work (Ammons, 1973) showed the usefulness of the 5-minute-boiling modification (Abruna and Vicente-Chandler, 1955) of the calcium hydroxide titration method applied to an acid sandy clay loam minesoil, as well as a satisfactory correlation ($r^2 = 0.84$) between lime requirement and values determined by the neutralization potential measurement.

The buffer method proposed by Shoemaker and others (1962) to determine lime requirement of soils with appreciable amounts of exchangeable aluminum is used by some agricultural soil-testing laboratories in northeastern United States. Although studies of acidic minesoils have shown significant amounts of soluble aluminum, we have not yet investigated applicability of the Shoemaker buffer method to minesoils.

PRACTICAL EXPERIENCES IN LIMING AND FERTILIZING

If a minesoil in the Appalachian region contains inorganic sulfur (greater than about 0.1 percent) that may produce more sulfate upon further weathering, lime in excess of immediate requirement may be necessary to neutralize this acidity and to prevent associated aluminum toxicity. If measurement of neutralization potential shows insufficient natural bases, an empirical estimate of lime requirement has been

useful, as follows: (immediate lime requirement) + (%S x 15) = tons of CaCO_3 needed per 1,000 tons of material (1,000 tons of earth material is approximately 1 acre of soil 7 inches deep or approximately 700 cubic yards of shattered overburden rock). The figure thus derived is about one-half of that theoretically required to neutralize the acid that can develop as calculated from pyritic sulfur. Because sulfates commonly account for 25 to 50 percent of the total sulfur in weathering minesoils, and because total pyrite weathering may occur only over a long time period, it is realistic to attempt to neutralize only a fraction of the calculated total by initial lime applications. On a practical basis, 5 tons per acre is the highest lime rate normally recommended for surface application. If the lime is to be incorporated into the minesoil to a 6-inch depth, rates of 10 tons or more may be used effectively. Rates as high as 87 tons have been tested (Sutton, 1973) with limited success, emphasizing that incorporation and time are both necessary in severe cases. Ammons (1973) showed that lime applied to the surface of an extremely acid sandy clay loam minesoil (pH 3.5 to 4.0) did not neutralize significantly below the 1-inch depth during 9 months of near-normal rainfall.

Soil tests for available plant nutrients in agricultural soils should be adaptable to evaluation of nutrients in minesoils, but tests may require adjustments to fit the chemistry of the particular material. Moreover, it should be noted that data indicating total chemical composition, as supplied by some commercial analytical laboratories, may be useless in estimating availability of elements for plant nutrition.

Nitrogen is rarely included in soil-test analyses, but the need for adding this element to disturbed land areas is normal where nonleguminous ground covers or forages are expected to thrive. Needs for nitrogen by grasses can be satisfied by periodic nitrogen fertilization or by emphasis on leguminous species in the planting mixtures. Probably the yields of grasses alone are limited primarily by deficiencies of nitrogen. Yield responses to four or more applications of 50 pounds (200 pounds total) of nitrogen per acre annually would be expected, depending on minesoil texture, rainfall, and interacting nutrients. However, establishment of legume-rich mixtures appears to be a more economical approach until the soil organic matter and nitrogen levels have been built up. With good stands of legumes, results suggest that buildup rate may be as rapid as 100 pounds of nitrogen per acre annually, whereas without legumes the rate may approximate 25 pounds

(Smith, Tryon, and Tyner, 1971).

Soil-test results, based on dilute acid extraction, for available potassium in most minesoils of West Virginia generally rate the supply as medium or high for crop production. The main reserves of potash-bearing minerals known to occur are micas, observable optically in sands and silts and identified by X-ray diffraction in clays. Because release from muscovite-type mica is known to be relatively slow, potash fertilization is likely to be necessary if high yields are to be achieved, unless biotite micas and feldspars comprise more of the potash reserves than is realized. In minesoils containing free carbonates it seems likely that some potash occurs in carbonate as well as in exchangeable forms, and acid extraction methods may give erratic results. In planned studies we expect to evaluate other extractants, including neutral salts, and to determine more precisely the modes of potash that occur.

Calcium and magnesium commonly are present in concentrations sufficient for diversified plant growth in minesoil and overburden materials that have appreciable base content as measured by the neutralization potential procedure. Acid materials, when limed sufficiently to eliminate severe acidity, will generally have enough magnesium as well as calcium to support vigorous forage growth, particularly if slightly dolomitic lime (where the ratio of calcium to magnesium is 20 to 1 or less) is used. However, extreme ranges of soluble magnesium, from less than 20 to more than 1,000 pounds per thousand tons, have been measured, and research is underway to identify the source of available magnesium. This is important because of the known association with low levels of magnesium in forage of grass tetany (West Virginia University, 1959) in cattle, as well as because of possible influences on grass yields.

Analyses for plant-available phosphorus, calcium, magnesium, and some trace elements can all be affected by peculiar interactions between the samples of overburden or minesoil and the chemical extractant used to evaluate the nutrient availability. For example, materials containing as little as 2 percent calcium carbonate can neutralize the acid contained in many soil extractants used in the eastern United States. In such cases the neutralized extractant cannot be expected to remove proportionate concentrations of nutrients that will correlate with field responses to fertilization. Concentrations of plant nutrients will be inaccurately estimated if the acid strength of the extractant varies from sample to sample or is completely neutralized.

Calculations of chemical equivalency show

that for the Bray No. 1 extractant, used for phosphorus fertility evaluation in several north-eastern states, where 1 g of sample is extracted with 10 ml of extractant that is 0.025N in hydrochloric acid, a sample containing 1.25 percent CaCO_3 will completely neutralize the acidity if all of the calcium carbonate is dissolved.

Field test application of dilute HCl shows that materials containing 2 percent CaCO_3 equivalent normally will "fizz" readily, providing a quick indication of a wide range of overburden and spoil materials whose soil-test results may be questioned. In addition it should be remembered that carbonates may be present even in acid minesoils that are too recently formed for chemical equilibria to be established.

Recent experiences suggest that evaluation of the available phosphorus status of minesoils, ranging from alkaline to extremely acid, can be accomplished by use of the sodium bicarbonate extraction method, which has been shown to correlate well with plant response in western United States, both with slightly acid and with alkaline soils (Olsen and others, 1954).

Because minesoils consist of various physically disrupted rock types, many of which contain fresh rock minerals, including carbonates and apatites, it is logical to expect that the sodium bicarbonate method will be an improvement over methods used previously to evaluate the phosphorus status.

Improved testing of minesoils for available phosphorus promises improved revegetation, reduced costs by avoidance of phosphorus fertilization which is not needed, and more accu-

rate longtime maintenance treatments on established vegetation.

INTERPRETATIONS AND CONCLUSIONS

Extreme acidity in certain minesoils derives from various forms of pyritic minerals. Intermediate acidity reflects hydroxy alumina on depleted layer lattice silicates. Desirable neutralizers generally are dominated by calcium, but include other alkaline earths and some alkalis in carbonate, silicate, and exchangeable forms. Meaningful extraction of available plant nutrients or biotoxins involves knowledge of pH, neutralization potential, and competing cations and anions. Physical properties depend on the strength and persistence of bonding between mineral grains in detrital rocks as well as on flocculating and soil-structure-forming interactions among fines.

Calcium quantitatively and qualitatively commonly exerts major physical influences. As a cation it flocculates colloids that might be dispersed by sodium. Exchangeable calcium, also, may provide interparticle divalent bridges favorable to soil structure. In excess of exchange, calcium carbonates effectively prevent colloidal dispersion and dilute extreme clay properties such as shrink-swell and stickiness. Moreover, in the presence of variable partial pressures of carbon dioxide, calcium carbonate will move and resegment during pedogenic processes, resulting in concretions, cemented peds, or horizons of concentration.

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CONTROL OF INDUSTRIAL SULFUR DIOXIDE EMISSIONS USING CARBONATE ROCK MATERIALS

by

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ABSTRACT

Electric-power-generating plants fired by fossil fuels are faced with increasingly stringent requirements for control of sulfur emissions. Several approaches for limiting these emissions, or for operating such facilities in an environmentally acceptable manner, are being pursued. Some of the approaches are based on the use of naturally occurring carbonate rocks or of materials derived from them. This paper discusses primarily the carbonate-rock-based processes being developed for control of sulfur dioxide emissions from fossil-fueled electric-power-generating plants. It includes a discussion of the role of carbonate rock materials in removal of sulfur dioxide from stack gases after combustion, capture of gaseous SO_2 during the combustion process, and removal of sulfur from fuel prior to complete combustion. Materials derived from carbonate rocks are generally used in processes which convert the sulfur to a throwaway product, but there are also proposed processes in which the sulfur is converted to a useful product and the absorbent is regenerated for reuse.

INTRODUCTION

Because of the increasing concern with protecting our environment and the need to meet legal obligations, electric-power-producing companies as well as other industries are engaged in extensive research programs to find and develop reliable methods for reducing sulfur emissions.

For the electric-power-producing industries that obtain their major portion of power from the combustion of high-sulfur coal (3.0 to 4.5 percent sulfur), the emission of sulfur dioxide as well as particulates is a major concern. In TVA, fossil-fueled plants account for over 80 percent of the generating capacity. Thus TVA has a direct interest in sulfur dioxide removal processes designed for this type of facility and is involved in numerous studies for sulfur emissions control as well as closely following other research in the industry. Based on available data from TVA and other sources, limestone

has shown good potential for reducing SO_2 emissions in wet-scrubbing processes and may be applicable in other methods used before or during the combustion process.

Chemically, limestone is mostly calcium carbonate, which will react with the sulfur dioxide present in the combustion gases to form an almost insoluble solid material, which can be removed from the gas. Limestone, under certain conditions, may also react with hydrogen sulfide (H_2S) gas. This is important for such processes as coal gasification, where the sulfur in the coal ends up as H_2S in the fuel gas produced. It has also been shown that limestone added to the combustion zone of a fluidized-bed combustion boiler will react with and immobilize the sulfur in the fuel and prevent its escape with the rest of the combustion gases. These are the three potential areas where the emission of sulfur can be reduced using limestone. The first process and probably the one that has had the most extensive study is flue-gas desulfuri-

zation utilizing wet-limestone scrubbing. Here the sulfur as SO_2 is removed after combustion. The other two proposed methods of sulfur removal take place in two of the more advanced concepts for combustion: the fluidized-bed combustion boiler and coal gasification. In the fluidized-bed combustion system, sulfur is removed during the combustion process; in coal gasification, it is removed from the low-Btu coal gas before complete combustion.

Before discussing these three potential processes, it would be helpful to gain an insight into the quantities of materials that will be required in treatment. For simplicity, I have chosen a 1,000-Mw coal-fired unit burning 3-percent-sulfur coal as an example. This size of unit and the sulfur content of the coal are not uncommon within the TVA system. For this generating capacity, a total of 400 tons of coal per hour would be burned. From this quantity of coal 12 tons of sulfur or 24 tons of SO_2 per hour are produced. For each pound of coal burned, 10 pounds of air are required for complete combustion. Thus large volumes of gases are produced; in fact, volumes amount to 4×10^6 ft³/min. The SO_2 content in this large volume of gas is approximately only 0.1 to 0.3 percent by volume. In order to effectively remove SO_2 from this large volume, equipment of considerable size must be used. On an annual basis, a unit of this size would burn 3×10^6 tons of coal; if limestone were used for sulfur emissions control, 300,000 tons of limestone per year would be consumed. In TVA alone, 35 to 40 million tons of coal are burned each year. If limestone-based processes were utilized for control of SO_2 then approximately 4 million tons of limestone would be required; hence limestone could become an extremely important commodity for SO_2 control.

REMOVAL OF SULFUR AFTER COMBUSTION— FLUE-GAS DESULFURIZATION WITH TAIL-END WET-LIMESTONE SCRUBBING

TVA's interest in this concept began in the early 1950's and later evolved into large-scale testing through a joint U. S. Environmental Protection Agency/Tennessee Valley Authority study which began in 1968. This study was made to test the application of dry-limestone injections in the boiler for the control of SO_2 emissions. Tests were conducted on a 175-Mw unit at TVA's Shawnee Steam Plant near Paducah, Kentucky. The process consists of injecting finely pulverized dry limestone into the boiler furnace, where

it is converted to calcium oxide, which in turn reacts with the sulfur dioxide in the combustion gases. The product formed is solid particles of calcium sulfate. The calcium sulfate and unreacted lime were removed in the same manner as fly ash.

The dry-injection process did not prove to be favorable for SO_2 control because of serious operating problems and low limestone-utilization efficiencies. The process resulted in boiler and superheater plugging and reduced the electrostatic precipitator efficiency. Also, when injecting limestone at unit stoichiometry (Ca/S mole ratio = 1), only 10 percent SO_2 removal was achieved. The EPA and TVA have abandoned this project and are now looking at tail-end wet-limestone scrubbing; however, Combustion Engineering (CE) took the process one step further and added a wet scrubber after injection. The first plant tested was at Union Electric's Meramec Station, but this plant has subsequently been shut down owing to operational difficulties. Additional systems were installed at the Kansas Power and Light Lawrence Station units 4 and 5 and Kansas City Power and Light Hawthorne Station units 3 and 5. Recently CE made a decision to convert these systems to a complete tail-end wet-scrubbing mode and is not promoting the limestone injection systems any longer.

Because TVA has operated a 1-Mw wet-limestone-scrubbing pilot plant since 1971 and, based on its operation, is constructing a full-scale (550-Mw) research and demonstration system, I chose this as an example for describing the limestone-scrubbing process. Figure 1 depicts the basic design and flow diagram for this system. This scrubber system consists of a Venturi which is used to cool, to saturate with water, and to remove fly ash from the flue gas. It should be noted that where effective electrostatic precipitators are used, the Venturi is not essential. Following the Venturi is the SO_2 absorber; for the system illustrated in figure 1 a grid tower is used, but the SO_2 absorber section can differ from system to system.

Some scrubber systems use only empty towers (no grids) and are called spray towers; others in conjunction with grids utilize various forms of packing to increase gas-liquid contact. In the system shown in figure 1 the slurry used for SO_2 absorption contains 10 to 15 percent solids, of which the major constituents are calcium carbonate, calcium sulfite, calcium sulfate, and fly ash. The slurry is pumped to the top of the absorber, where it is sprayed countercurrent to the gas flow and discharges out of the scrubber into a circulating tank. From here it over-

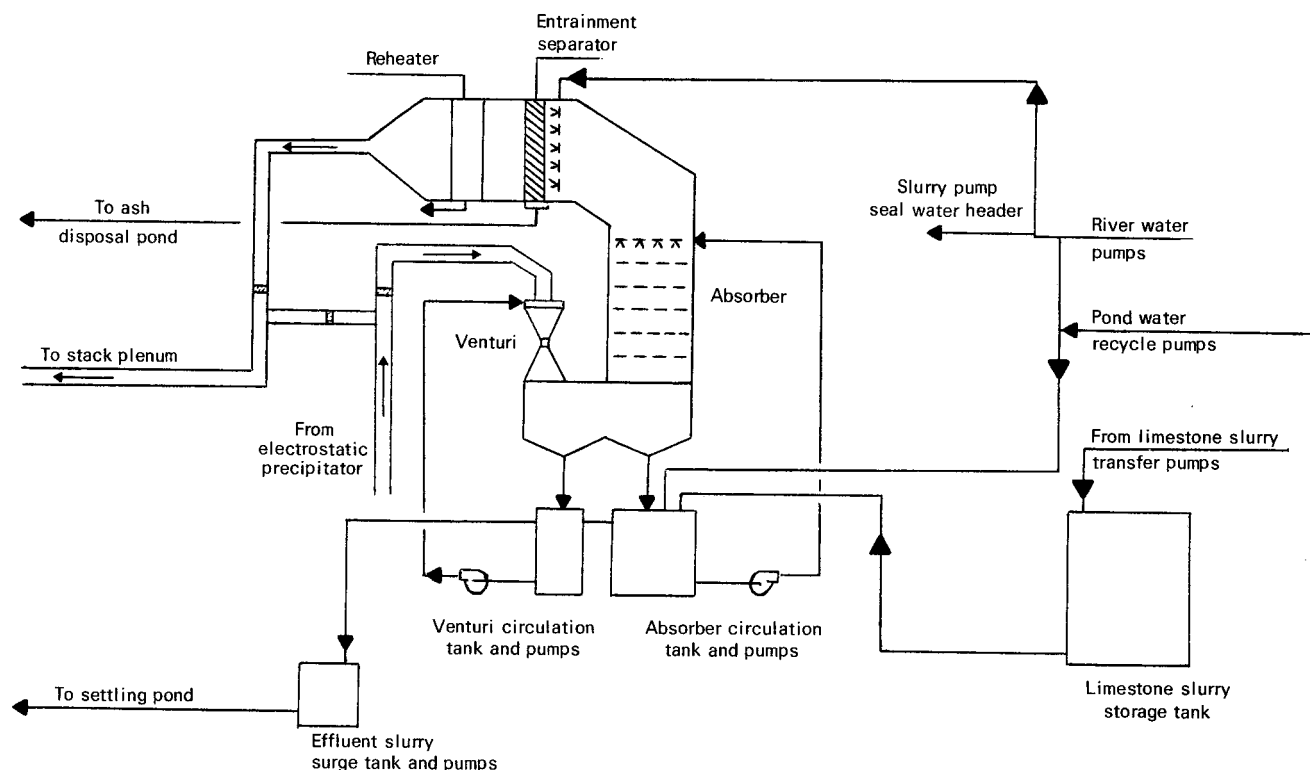


FIGURE 1. - Scrubber-system flow diagram.

flows into the Venturi circulation tank, from which it is pumped to the Venturi scrubber. Spent scrubber material is removed from the Venturi circulation tank and the system and is sent to a disposal pond; supernatant liquor is returned to the system. Limestone which is ground to 90 percent 200 mesh is added at a Ca/S mole ratio of 1.2 to 1.5 based on inlet SO₂ concentrations; SO₂ removal efficiencies range from 70 to 80 percent. This type of system is not without problems. Deposits of insoluble calcium sulfate material in the flue-gas scrubber and scaling and plugging in the mist eliminator have caused problem areas. In addition, serious problems arise with equipment due to corrosion, erosion, poorly designed components, and failure of the solids produced to settle satisfactorily in the disposal pond. Extensive work is now being conducted in finding ways to solve these problems.

From a recent evaluation of the wet-limestone systems that are now installed on full-scale units and those committed for the near future, it seems that by 1977 a minimum of 17,000 Mw of generating capacity will be connected to wet-limestone scrubbers in the United

States; there are, however, competitive processes that do not utilize limestone. Some of these systems are the MgO process offered by Chemico, the Cat Ox process offered by the Monsanto Chemical Company, the Foster Wheeler dry-absorption process, the molten salt process being developed by Atomics International, the sodium process offered by Davy Power Gas, and others. These processes recover sulfur in some potentially useful form, but seem to be more complex and require process equipment that the simpler limestone-throwaway processes do not.

Systems are also being developed which will utilize limestone indirectly. The wet-lime-scrubbing processes are good examples of this. Double alkali systems utilizing limestone or lime to regenerate soluble spent scrubber material such as sodium or ammonium sulfate and sulfite are also being developed.

There are many other potentially attractive stack-gas SO₂-removal processes beyond these already mentioned, but the ones that utilize limestone directly or indirectly have had more extensive study and probably provide the greatest potential for the largest application.

REMOVAL OF SULFUR DURING COMBUSTION—DESULFURIZATION IN A FLUIDIZED-BED COMBUSTION BOILER

The fluidized-bed combustion process is being studied on the basis of its potential for providing significantly higher power-plant efficiencies; efficiencies are now, for conventional boiler systems, on the order of 38 percent. These types of systems should be classified as research in combustion technology for the electric-power industry. The basic design of such a system and how it is integrated with the production of power is shown in figure 2. There are basically two types being studied—the atmospheric system and the pressurized system. The operation of these systems and the sulfur removal step will be discussed as a single operation.

For combustion of coal and for SO_2 removal, a fluidized-bed boiler utilizes a bed composed of a mixture of crushed coal and limestone and fluidized by compressed air flowing up through a distribution plate located beneath the bed. An important element of the fluidized-bed combustion boiler is the presence of boiler tubes submerged in the bed to produce steam from the heat produced in the combustion process. The

fluid bed operates at a temperature of 1400° to 1900°F . This is well below the ash fusion temperature and at the right temperature for the limestone-sulfur reaction. Thus SO_2 produced by combustion can be chemically combined with the limestone in the combustion zone to form calcium sulfate. Most of the calcium sulfate and unreacted limestone are retained in the bed and removed from the furnace with the ash. For electric generation the main difference in the atmospheric and pressurized systems is that in the pressurized system (approximately 10 atmospheres) the boiler can be connected not only to a steam turbine but also to a gas turbine; thus the pressurized system becomes more efficient than the atmospheric system. Also, the combustion efficiency in atmospheric beds has been low (approximately 88 percent), whereas the combustion efficiency in the pressurized units has been on the order of 99.5 percent.

A study by Battelle Columbus Laboratories indicated that in the atmospheric beds a Ca/S mole ratio of 4 was required to remove 85 percent of the sulfur. This amounts to about 200 pounds of limestone per 400 pounds of coal; but in the pressurized beds, Battelle found that dolomitic limestone was superior for sulfur removal,

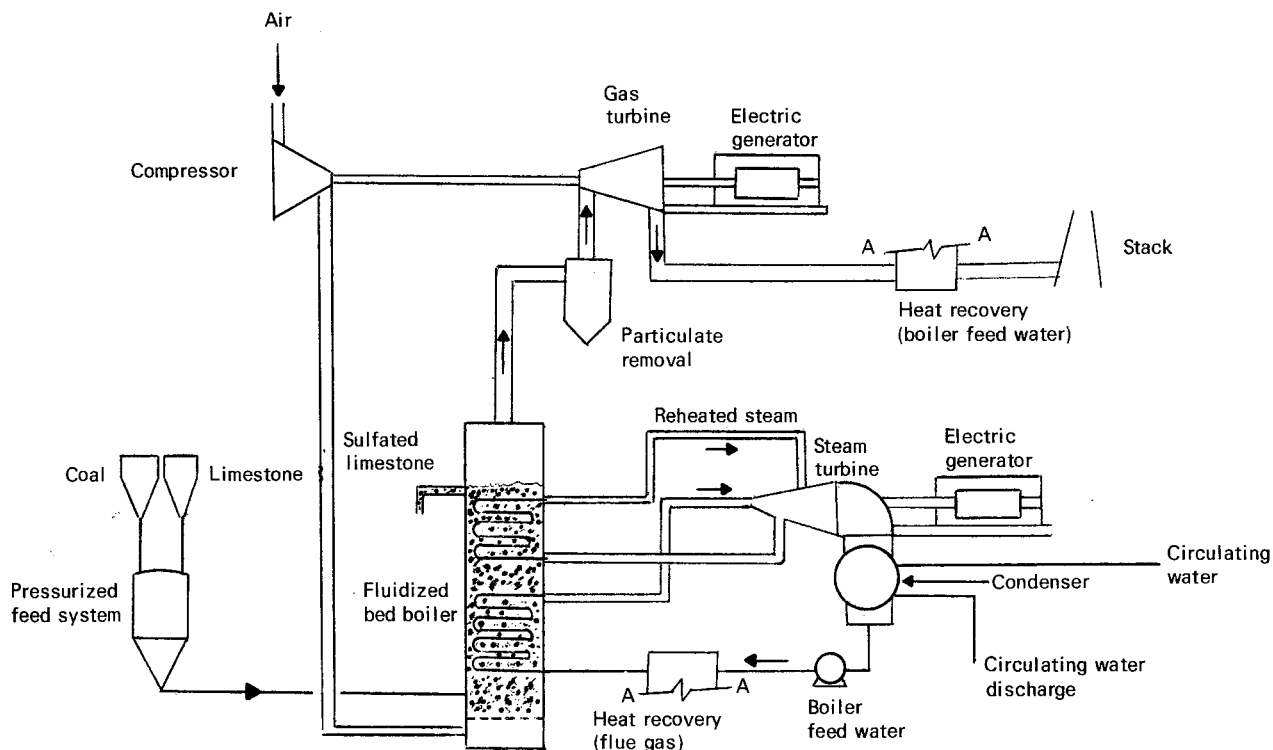


FIGURE 2. - Pressurized fluidized-bed boiler power plant.

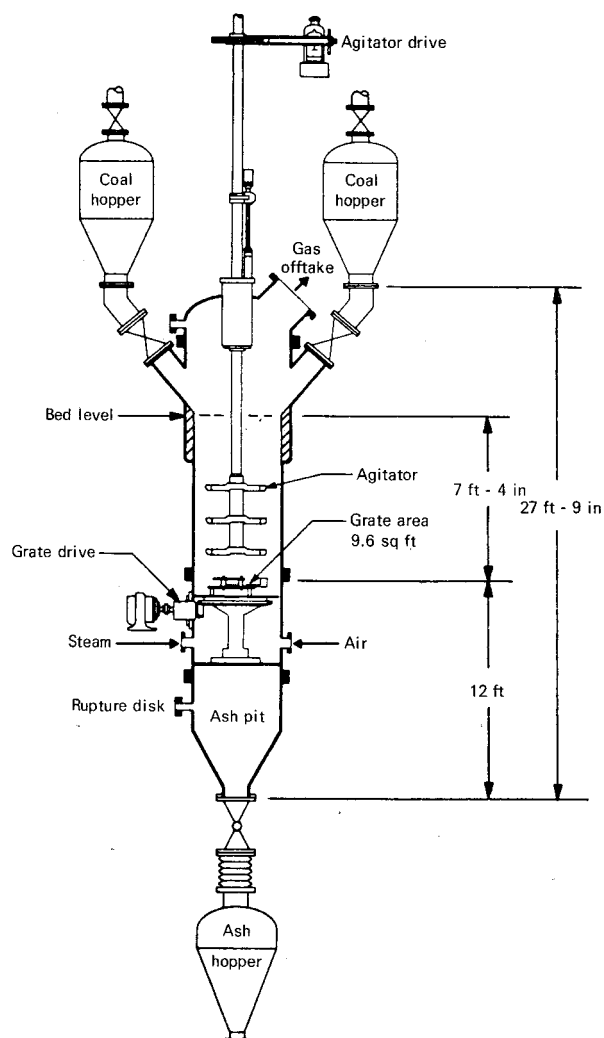
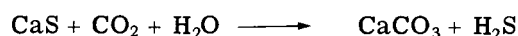


FIGURE 3. - Schematic drawing of a gasifier.

and that greater than 85 percent sulfur removal was obtained when a Ca/S mole ratio of 1.6 to 2.0 was used. It is still desirable to reduce this limestone requirement to a mole ratio of 1.2 or less. These stoichiometric ratios are based on what leaves the system and not on what is actually in the bed.

It has also been proposed that the calcium sulfate may be processed to elemental sulfur. This process would also regenerate limestone so that it could be returned to the furnace. The regeneration schemes would follow the following reaction:



The H_2S would later be taken to a Claus unit for the production of elemental sulfur.

No determination has been made at this time whether the regeneration schemes are technically or economically feasible. Thus initial pilot-plant testing of fluidized-bed combustion boilers will probably be conducted without regeneration of the limestone.

REMOVAL OF SULFUR BEFORE COMPLETE COMBUSTION—DESULFURIZATION IN COAL GASIFICATION

The approach of removing sulfur before the completion of combustion appears attractive because the volume of gas that requires treatment is substantially less than that noted under flue-gas desulfurization. This is one of the main reasons coal gasification is being considered for the power-producing field. In fact, it is being considered as an alternate to stack-gas desulfurization.

In coal gasification the gases are produced in a vessel in which coal is heated and partially reacted with air and steam to produce the combustible constituents CO , H_2 , and some methane. The amount of air used in gasification is only about a third of the amount required for complete combustion of coal. As a result of this oxygen-lean mixture, the sulfur evolves as H_2S from the gasifier rather than SO_2 . Figure 3 is a schematic drawing of a gasifier.

As in the case of the other two processes discussed in this paper, a calcium compound such as limestone or dolomite may be used to remove the gaseous sulfur. Although this reaction with H_2S occurs to a significant extent only at temperatures of about 1000°F , this does not pose undue restriction for the calcium application because the temperature of the gasification products is generally in the range of 1000° to 1800°F .

The work performed by Westinghouse on the development of a fluidized-bed gasifier will probably demonstrate the first practical use of calcium in removing sulfur during coal gasification. In the Westinghouse 1,200-lb/hr process demonstration unit (which is soon to become operational), a bed of limestone and coal ash is maintained "fluid" (or suspended in a turbulent mixture) by the injection of steam and air at the bottom of the containment vessel. Coal is also injected into the bed, where it is quickly heated by the intimate contact with the hot limestone while reacting with the air and steam to produce the primary gaseous fuels CO and H_2 . The sulfur evolved from the coal reacts with the limestone to produce calcium sulfide and sulfate. A solids stream is continu-

ally withdrawn from the bed for disposal of spent limestone and ash or possibly for regeneration of the limestone for reinjection to the gasifier. The details of the gasifier design can be found in the literature. The point to be made here is that calcium serves as a sulfur absorption medium in what is considered to be one of the more advanced coal-gasification concepts.

Recently the U. S. Bureau of Mines tested the potential of inherent H_2S absorption in a gasifier by mixing limestone chips with coal and feeding the mixture to a $3\frac{1}{2}$ -foot-diameter experimental fixed-bed gasifier (a gasifier operating much like a pot-bellied stove). The results of an exploratory test indicate that sulfur absorption with limestone in the fixed bed is possible and can result in at least 50 percent sulfur reduction in the product gas.¹

An alternative to the inherent sulfur absorption within the gasifier bed is to perform the desulfurization after the gases leave the gasifier. The Bureau of Mines has performed tests in which the hot gases from the gasifier are passed through a fixed limestone bed. The experimental results, however, are disappointing because it appears that the limestone becomes covered and plugged with what may be cracked tars produced in the gasifier. Plugging of the limestone bed thus prevents the continued effective absorption of H_2S . The hot limestone bed, however, may still have applications for those gasifiers in which the gases evolve at temperatures above the point in which the tars can exist. The temperature limitation in this case is the softening or melting point of limestone.

The primary measures for desulfurizing the

gas stream are those which operate at temperatures below 200°F. The development of a hot gas cleanup such as the Lurgi hot carbonate system is important from the standpoint that such systems do not incur the 15 to 20 percent heat losses usually associated with cooling the gases to such low temperatures. The successful application of the limestone processes, however, still involves extensive development to realize both their technical and economic feasibility.

SUMMARY AND CONCLUSIONS

In utilizing limestone to control emission of sulfur, the successful application of processes such as flue-gas desulfurization, the reaction of limestone with sulfur in coal gasification, and fluidized-bed combustion boilers still involves development to realize both their technical and economic feasibility. Also, the disposal of solids produced in these systems may be a major obstacle to acceptance by the utility industry if some form of utilization or regeneration is not found.

Of the three processes discussed, flue-gas desulfurization has had the most extensive research study and testing on the largest scale. Even now, some of these systems have been installed or are being installed on full-scale units. Thus this type of sulfur-control equipment will produce the initial demand for limestone. The performance of these full-scale scrubber systems will dictate their future use and acceptance in the industry.

Based on a recent Federal Power Commission estimate, by the year 1975 about 40 million tons of limestone could be utilized for sulfur emissions control from the production of electric power alone. Other industries would require about a fourth of that amount. So from the work presently being conducted in using limestone for the control of sulfur emission and the quantities of limestone that would be required for these systems, it seems that limestone has a very good potential in the pollution control area.

¹Limestone chips were $\frac{1}{2}$ inch in size, and in 25 percent concentration in the coal feed mix. The Pittsburgh seam coal used contained $3\frac{1}{2}$ percent sulfur. The resulting H_2S concentration in the gas was 0.15 to 0.3 percent. The gasifier calcines limestone to lime, releasing CO_2 . Bottom ash analysis showed sulfur present as calcium sulfate and sulfide.

CARBONATE ROCK PROPERTIES REQUIRED BY DESULFURIZATION PROCESSES

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ABSTRACT

Because of their relatively low cost, carbonate rocks are desirable in abatement of air pollution by acid gases. Although many processes and types of equipment have been proposed to control or prevent the emission of acid gases, this paper considers only three: dry-limestone injection, wet-limestone scrubbing, and chemically active fluid beds.

For the dry-limestone-injection process, surface area—especially from pores in the 0.2- to 0.3-micron range—is one of the important parameters which will discriminate between less and more reactive carbonate rocks. Marls, chalks, oolitic calcites, and other fine-grained limestones show larger-than-average surface areas and better-than-average removal efficiencies. Inert chemical impurities such as silica detract from reactivity. A dolomite is not necessarily less reactive than a calcite.

For the wet-limestone-scrubbing process, dissolution rate of the carbonate rock controls the differences in stone reactivity. In this process the dolomites are less reactive than the calcites. In addition, more than 90 percent of the dolomitic impurity in Fredonia white limestone is inert during limestone scrubbing. Dissolution rate is also a function of particle size for large-grained carbonate rocks. Fine grinding of such rocks will increase the dissolution rate to that of a fine-grained rock. Hence the requirement of high dissolution rates may be met by some grinding of fine-grained material (e.g., marl, chalk, or other limestone) or by fine grinding of coarser grained material.

For chemically active fluid beds, chalks have the best capacity to absorb both SO_2 and H_2S . However, most chalks are probably unsuitable for fluid beds because of high attrition rates. Because dolomites are generally more reactive than calcites with both SO_2 and H_2S , a dolomite would be the feed material of choice for a chemically active fluid bed.

INTRODUCTION

Because of the relative low cost of carbonate rock materials, air-pollution abatement of acid gases is more attractive utilizing carbonate rocks. Although a great many processes and types of equipment have been proposed to control or prevent the emission of acid gases, this paper will consider only the following: (1) dry-limestone injection, (2) wet-limestone scrubbing, and (3) desulfurizing-fluid beds. The first, dry-limestone injection, is discussed because a demonstration project for this process has been completed and because the process illustrates some important properties which affect carbonate-rock characterization. Several variations of the wet-limestone-scrubbing process have been and are being tested in demonstration projects and appear to be suitable for abatement of sulfur oxides emissions at this time. The desulfurizing-fluid bed is used in more advanced processes, such as coal gasification or fluidized-bed combustion. The last two processes both remove sulfur oxides before they reach the stack and allow a more advanced and long-term solution to the control of sulfur oxides.

DRY-LIMESTONE INJECTION

The dry-limestone-injection process was evaluated in a full-scale demonstration of performance at the TVA Shawnee Steam Power Plant, Paducah, Kentucky. Optimum conditions for sulfur dioxide abatement were determined, as well as effects on operation of the power plant and economics of the process. Under the process evaluation planned by TVA (1968) carbonate rock (limestone or dolomite) was ground to 70% less than 200 mesh and was injected above the fireball at points where the temperature was from 2400° to 2900°F. The carbonate rock calcined (evolved carbon dioxide), and the resultant lime reacted with the sulfur oxides in the presence of oxygen to form calcium sulfate. The calcium sulfate was removed with the fly ash in standard dust-collection systems. The results of this demonstration were published by the Control Systems Laboratory, Office of Research and Development, EPA (Tennessee Valley Authority, 1973) in a comprehensive three-volume set. Requirements for carbonate-rock feed materials were found to relate to the fact that the temperature of injections had a major impact on the reactivity of the carbonate rock. Injection locations initially chosen gave rise to deadburning (Drehmel, 1970), and locations at lower temperatures* (e.g., 1800°F) deprived

the rock of sufficient residence time at high temperatures to react with the sulfur oxides. It was determined that the optimum injection temperature was 2100°F. Three carbonate rock materials were tested:

1. An oolitic high-calcium limestone—Fredonia white limestone (FWL) (Mississippian, part of Fredonia Member, Ste. Genevieve Limestone, Fredonia, Kentucky)
2. A bog marl—Vorres Michigan marl (VMM) (Pleistocene, fresh-water deposit)
3. An oolitic aragonite—Bahama aragonite (OBA) (Pleistocene, marine sand deposit)

A complete petrographic description of these rocks is given by Harvey (1971). Sulfur oxide removal efficiency for all three of these additives was low (*i. e.*, approximately 10% SO₂ removal per unit stoichiometry) under normal boiler operating conditions. However, important differences between these materials were observed. For example, the residence time for reaction could be increased by reducing boiler load to 75 Mw as opposed to the normal 140-Mw load. At a 75-Mw load, marl was significantly more efficient in removing SO₂. At an addition rate of three times the stoichiometric amount, the removal of SO₂ for marl (VMM) would be approximately 48%, for the calcite (FWL), 36%, for the aragonite (OBA), 26%. This difference is attributed to the ability of VMM to improve with increased residence time, whereas FWL and OBA leveled early. This difference, in turn, is related to the surface area available for reaction and the rate at which surface area is lost because of formation of reaction products. Because surface area increases with decreasing pore size, the reactivity of the carbonate rock will be greater if it has more fine pores. However, it appears that pores smaller than 0.1 micron are quickly blocked by reaction products. Hence the requirement for the carbonate-rock feed material is that it have a large surface area from pores in the 0.2- to 0.3-micron range. This requirement is met by many fine-grained (*i. e.*, having small crystallites) limestones and by marls and chalks.

*Although it is the policy of the EPA to use the metric system for quantitative descriptions, the British system is used in this paper. Readers who are more accustomed to metric units are referred to the conversion factors as follows:

- (1) °F to °C, subtract 32 then divide by 1.8
- (2) cfm to m³/hr, multiply by 1.70.

WET-LIMESTONE SCRUBBING

One of the SO_2 -abatement processes most actively considered for immediate installation is limestone scrubbing. Limestone scrubbing may be classified according to the mode of limestone addition. For example, in the limestone-injection-scrubbing process just described, the limestone is injected into a region of the steam/electric power boiler where it will calcine. Traveling through the boiler, the newly formed lime reacts partially with SO_2 in the flue gas before entering the scrubber, where the remaining SO_2 is removed. In the limestone tail-end-scrubbing process, finely ground (95% of which is 74 microns or smaller) limestone is added directly to the scrubber circuit. In the lime tail-end-scrubbing process, limestone is calcined external to the power boiler and either calcium oxide or hydroxide is added directly to the scrubber circuit.

Besides the many variations in the form and addition point of the alkali, several types of scrubbers are being considered: (1) open scrubbers such as Venturi, Venturi-rod, inspiration, and spray tower; (2) partially open scrubbers using a sieve, perforated plate, or mobile bed; and (3) packed towers. Among the mobile-bed scrubbers are the turbulent-contact absorber (TCA) and the hydrofilter or marble bed.

Various combinations of types of contactors and modes of limestone addition have been and are being tested or installed. One of particular note is at the TVA Shawnee Steam Plant. Three 30,000-cfm scrubbing trains were installed to operate on a side stream of Unit #10. The three scrubbers installed were a marble bed, a TCA, and a Venturi in combination with a spray tower. To date the bulk of the testing at Shawnee has been with limestone addition to the scrubber circuit, although the lime-scrubbing mode is now being investigated. Results of the lime/limestone-tail-end-scrubbing experiments were presented recently at a briefing for industry (Bechtel Corporation, U. S. Environmental Protection Agency, and Tennessee Valley Authority, 1973). The limestone used throughout these tests was high-calcium oolitic limestone (FWL) which had been used in the dry-limestone-injection process demonstration. Because no other stone was tested, requirements for limestone type cannot be inferred directly. However, a strong dependence of limestone reactivity on particle size (or grindability) was observed at Shawnee. Also, use of dense and dolomitic beds from the source quarry resulted in decreased SO_2 sorption efficiency compared to that for the

beds of porous oolitic limestone. The particle size effect was studied in detail at the EPA pilot facility at RTP. This facility consists of two 300-cfm scrubbers fed with flue gas from a natural-gas/oil-fired boiler. Sulfur dioxide levels of 3,000 ppm were maintained by doping the flue gas from cylinders. The RTP scrubbers operate with a closed loop, using a rotary drum filter for solids disposal. Using this apparatus, it was found that the rate of CaSO_3 precipitation is controlled by and directly related to the CaCO_3 dissolution rate, which is controlling for the SO_2 -scrubbing process. Hence the performance of the limestone scrubber can be followed by observing the CaSO_3 precipitation in the effluent hold tank. Two distinct particle-size distributions were tested: 7% greater than 325 mesh (44 microns) and 16% greater than 325 mesh. At a given SO_2 concentration in the liquid phase, it was found that the rate of sulfite precipitation for the smaller particle size was twice that for the larger particle size. As at Shawnee only one type of stone, FWL, was tested at RTP. However, comparisons of limestone types have been made in other tests at the pilot-plant size. Among the scrubbers used in these tests were a Venturi, a packed-bed, and an inspiration-type scrubber. The packed-bed scrubber was part of a 1,000-cfm pilot plant using a flooded-disc Venturi scrubber followed by the wetted-film packed tower (Gleason, 1971). Using the limestone-tail-end process, the SO_2 removals in the tower were as follows:

1. Cement dust: 73.5%
2. Calcite (75%, -200 mesh): 81.6 to 88.4%
3. Calcite (89%, -325 mesh): 95.1%
4. Chalk (89%, -200 mesh): 96.6%

The inspiration-type scrubber was part of a 1,500-cfm limestone-tail-end process (Craig, Bell, and Fayadh, 1971). The SO_2 removals using 1% slurry compared as follows:

1. Dolomite: 46.8%
2. Calcite: 74.8%
3. Coral marl: 74.6%
4. Precipitated carbonate: 78.3%
5. Calcium oxide: 93.1%

The SO_2 removals averaged over runs using 1% to 5% slurry were 72.3% with calcite and 74.7% with coral marl.

The Venturi-scrubber pilot tests used a two-stage Venturi handling 1,500 cfm (Shah, 1971). Among the alkalis tested were 14 calcitic carbonates, 5 limes, 1 dolomite, 1 dolomitic lime, and 1 carbide sludge. Neither sources of nor petrographic information about the calcitic carbonates were given. In comparison of SO_2 removals among the calcitic carbonates, the spread between

TABLE 1. - Chemical analysis in weight percentage and petrographic characteristics

Sample type number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	CO ₂	Mineralogy*	Petrographic type
1	nil	nil	nil	nil	55.3	43.95	Calcite	Iceland spar rhombs
2	nil	0.01	0.19	nil	55.5	43.95	Calcite	Spar
3	nil	nil	0.20	1.86	53.4	43.75	Calcite (dolomite)	Coarse limestone
4	1.53	0.01	0.31	nil	54.8	43.35	Calcite (quartz)	Fine limestone
5	0.03	0.02	0.34	21.40	30.30	47.30	Dolomite	Reef dolomite
6	11.8	1.77	0.13	17.4	26.5	40.27	Dolomite (quartz, clay)	Non-reef (impure) dolomite
7	0.47	0.08	nil	44.2	2.93	50.96	Magnesite	Fine magnesite
8	0.19	0.27	nil	nil	55.2	42.10	Aragonite	Oolitic sand
9	5.88	0.69	2.82	15.33	30.82	40.68	Dolomite (calcite, quartz)	Calcitic dolomite
10	0.85	0.20	0.15	1.4	53.7	43.4	Calcite (tremolite)	Marble
11	3.63	0.95	nil	nil	46.6	37.18	Calcite (quartz, clay)	Bog marl
12	2.48	1.09	0.15	1.41	51.4	39.44	Calcite	Chalk

*Minor mineral constituents given in parentheses.

the best and worst under a given set of conditions was as little as 11 and as great as 20 percentage points in SO₂-removal efficiency. In particular, the SO₂ reduction using two 90%-plus calcium carbonate rocks was 60% for the first and 80% for the second; a 90% minus 325-mesh stone was used in both cases.

These pilot-plant results may be compared to laboratory measurements of dissolution rate by titration (or simply titration rate). The titration rate was determined using 1-g samples of specific particle sizes, slurried in 200 ml of distilled water and titrated with 0.20N sulfurous acid. The titration rate was adjusted continuously to bring the slurry pH down to, and hold it at, the desired point. Quantities of acid consumed were recorded at 1-minute intervals, and the equivalents of acid consumed per time were calculated. The carbonate rocks tested are described in table 1.

Titration rates for the 12 carbonate rock types tested are given in table 2. In one case the data were obtained at pH 4, 70°F, with 16/20-mesh material; in the other, pH 6, 110°F, with 270/325-mesh material. The former is a convenient test condition; the latter is very close to conditions used in a scrubbing process. In general, chalk and marl are the best and dolomites the worst. The effect of particle size on titration (fig. 1) points out an important difference between fine- and coarse-grained carbonate rocks. The dissolution rate for the fine-grained material (T-12) is consistently high; that for the coarse-grained material (T-3) be-

comes greater as the stone is ground finer, until there is little difference between the two.

The poor performance of the dolomites in the dissolution-rate experiments is in agreement with the results on the inspiration-type pilot scrubber noted above. During tests using the

TABLE 2. - Titration rates of carbonate rocks

Type	Description	Titration rate (milliequivalents per minute)*	
		pH 4	pH 6
1	Iceland spar	0.12	0.11
2	Calcite spar	0.10	0.11
3	Coarse-grained limestone	0.27	0.28
4	Fine-grained limestone	0.27	0.29
5	Reef dolomite	0.04	0.03
6	Non-reef dolomite	0.14	0.05
7	Magnesite	0.00	0.08
8	Aragonite, oolitic sand	0.84	0.32
9	Calcitic dolomite	0.04	0.06
10	Marble	0.08	0.18
11	Marl	>3.0	0.29
12	Chalk	>3.0	0.37

*If pH 4, 70°F and 16/20 mesh; if pH 6, 110°F and 270/325 mesh.

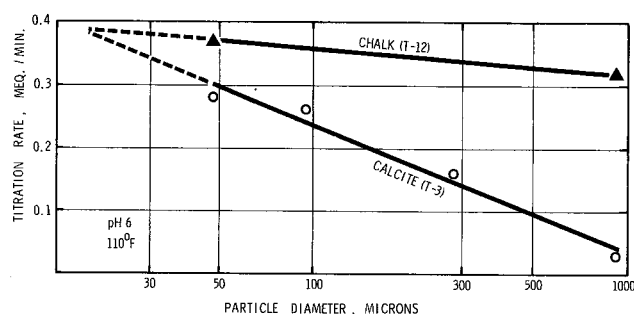


FIGURE 1. - Effect of particle size on titration.

EPA pilot plant at RTP (also noted above) no dolomitic carbonate rocks were tested. Very accurate chemical analyses of the various liquor streams and precipitates did allow observations of the fate of the dolomitic impurity in FWL, the carbonate rock tested. It was found that less than 10% of the dolomitic portion dissolved during the scrubbing process. The remainder was inert and did not contribute to the SO_2 -removal reaction.

Requirements for the carbonate-rock feed material for wet-limestone scrubbing may be deduced from the above. Since the dissolution rate is a rate-controlling step for the SO_2 -removal process, a stone with rapid dissolution is central. The carbonate rock should be ground finely for high dissolution rates. Where soft fine-grained materials may be used, grinding costs will be lower and the particle-size distribution will be shifted to the fines. Among the carbonate rock types, dolomite is the least reactive and precipitated carbonate the most. Marls and chalks are slightly better than other calcites. Recent tests have indicated that pulverized aragonitic clam shells from coastal deposits have extra high rates of dissolution in an aqueous solution with 5,000 ppm SO_2 bubbling through it at 500 $\text{cm}^3/\text{minute}$. Also calcite waste sludges from certain industrial plants have relatively high dissolution rates. However, the effect on operating reliability of various stone types has not been studied.

DESULFURIZING-FLUID BEDS (OXIDIZING CONDITIONS)

Certain carbonate rocks have been tested in pilot plants of desulfurizing-fluid beds used in fluidized-bed combustion of coal. In these tests crushed limestone or dolomite has been added to the combustion chamber to react with

the SO_2 produced from the fuel. This process and the experiments are described in detail in reports to the EPA (Jonke and others, 1971; Robison and others, 1970). The central differences between fluidized-bed combustion of coal and other forms of coal combustion are the presence of the boiler tubes in the bed and high heat-transfer coefficients. With this configuration the combustion zone stays in the 1600° to 1900°F range so that limestone can be used without dead-burning. Problems experienced in these tests, associated with the carbonate-rock additives, were excessive attrition of particles of certain samples by decrepitation or breakage during high-temperature treatment and excessive agglomeration during the lime-regeneration cycle.

Batch fluidized-bed tests of McConville, Inc., dolomite (MCD) gave relatively high attrition rates; Warren Bros. dolomite (WBD) and Denbighshire stone (DEN) gave low attrition rates (Craig and others, 1971). In addition, the tests showed excessive agglomeration of sample MCD. During subsequent continuous pilot tests, WBD showed some agglomeration and greatly increased rates of attrition.

As the attrition of limestone particles by decrepitation is routinely evaluated by glass manufacturers, the samples were tested using the same procedure (Jay Bitner, Ball Corporation, Mundelein, Illinois, private communication, 1973). The test measures the relative amount of crushed sample that explodes over the sides of a sample container (long thin boat) during exposure to 1100°C. Test results of the samples studied at the Illinois State Geological Survey are given in table 3. These results are in agreement with the results of relative attrition in some batch fluidized-bed tests; however, no general correlation is apparent. The mineral, chemical, and petrographic properties of the four samples differ widely. Two, MCD and TYD (Tymochtee Dolomite), are dolomites, and the other two are limestones. Impurities are mainly siliceous quartz, clay, and feldspar; the last is especially abundant in sample MCD, accounting for the observed agglomeration of regenerated calcine particles of the dolomite. Feldspar begins to fuse at 1100°C; in the manufacture of glass this mineral is used as a flux to reduce the eutectic temperature of silicate mixes. During the process of regeneration of the calcine, sulfated calcine particles are heated to 1100°C, and it is at this point that the feldspar, especially the finer grained feldspar, partly fuses and causes the undesirable agglomeration.

The relative abundance of defects within the carbonate grains appears to correlate well with the decrepitation observed when the glass manu-

TABLE 3. - Petrography, pore structures, and decrepitation test results

	Sample rock type*			
	MCD Dolomite, sandy and calcitic	TYD Dolomite	WBD Limestone, dolomitic	DEN Limestone
Mean grain chord (μ)	47	19	4	10
Grain defects**				
Point	1, 678	987	407	659
Line	129	30	15	62
Pore volume (cc/g)	0.0084	0.0250	0.0056	0.020
Calcine:				
Pore volume (cc/g)	0.150	0.210	0.192	0.200
Mean pore size (μ)	0.039	0.051	0.110	0.060
Pore volume increase (cc/g rock)	0.142	0.185	0.186	0.180
Theoretical increase (cc/g rock)	0.145	0.182	0.174	0.182
Surface area (m ² /g rock)	13.8	13.9	4.9	13.9
Decrepitation (%)	3.67	0.23	0.0	3.68

*MCD, McConville, Inc., Ogdensburg, New York, TYD, C. E. Duff & Sons, Huntsville, Ohio (Tymochtee Dolomite), WBD, Warren Bros. Road Construction, Syracuse, New York, DEN, Denbighshire, Northern Wales, United Kingdom.

**Number in 100 carbonate grains that are $>50\mu$ diameter times percentage of $>50\mu$ grains in sample.

facturer's test was made. The defects in the two dolomites and in the dolomitic limestone (MCD, TYD, and WBD) are mainly point defects. Increases in point defects in these samples correspond to increasing decrepitation. The presence of line defects within the sparry calcite grains of DEN contributes to fracture propagation through the rock and thereby reduces its hardness and decreases its resistance to attrition. In actual fluidized-bed tests, MCD, which has the most defects, had the greatest attrition rate. However, attrition of WBD and DEN was strongly dependent on other parameters (such as SO₂ concentration and temperature), so that no correlation with defect structure is obvious.

Another consideration in carbonate-rock requirements for desulfurizing-fluid beds is the capacity of the stone to react with sulfur oxides. Experiments and results for different types of stones have been reported by EPA (Borgwardt and others, 1971) in terms of the grams of SO₂ (expressed as SO₃) absorbed per 100 g of calcined stone. The results were as follows:

Iceland spar	17.3
Magnesite	19.7

Marble	32.0
Calcite	32.7
Dolomite	43.8
Aragonite	52.1
Oolite	57.1
Chalk	66.4

DESULFURIZING-FLUID BEDS (REDUCING CONDITIONS)

Desulfurizing-fluid beds may also be used in reducing conditions, as found in some part of a coal-gasification process (Lemezis and Archer, 1973). Requirements for resistance to attrition and decrepitation in this case would be much the same as those in oxidizing conditions. The capacity for reactions, however, would be between carbonate rock and H₂S. The U. S. Bureau of Mines has evaluated materials for their reactivity with H₂S by exposing pellets of the test substance to producer gas at 1000° to 1500°F (Shultz and Berber, 1970). At the request of EPA, a variety of carbonate rocks were also tested at the Bureau of Mines and the results, according

to type, in terms of percent sulfur weight gain, are:

Marl	2.1
Calcite	13.1
Dolomite	14.4
Chalk	18.0

It should be noted that chalk had the highest capacity for both SO_2 and H_2S . Hence where a chalk which has suitable decrepitation and attrition resistance may be located, its performance should be most suitable for a desulfurizing-fluid bed. For both SO_2 and H_2S capacity, the dolomites were more reactive than calcites. As noted earlier, there are properties of dolomites which may be avoided to alleviate decrepitation or agglomeration problems. Consideration has been given to the use of calcines of carbonate rocks as desulfurizing agents in fluidized beds operating under reducing conditions. Half-calcined dolomite ($\text{CaCO}_3 \cdot \text{MgO}$) was found to desulfurize H_2S gases with greater reactivity and at a faster rate than fully calcined dolomite (Ruth and others, 1972); CaS is the reaction product from these experiments, which were run at temperatures of 550° to 800°C at various levels of CO_2 . Half-calcined dolomite was evaluated for use in three varieties of fluidized-bed gasifiers.

SUMMARY OF CONCLUSIONS

For the dry-limestone-injection process, surface area—especially from pores in the 0.2- to 0.3-micron range—is one of the important parameters which will discriminate between less and more reactive carbonate rocks. Marls,

chalks, oolitic calcites, and other fine-grained limestones show larger-than-average surface areas and better-than-average removal efficiencies. Inert chemical impurities such as silica detract from reactivity, but any given dolomite is not necessarily less reactive than any given calcite.

For the wet-limestone-scrubbing process, dissolution rate of the carbonate rock controls the differences between stone reactivities. In this case the dolomites are less reactive than the calcites. In addition, more than 90% of the dolomitic impurity in Fredonia white limestone is inert during limestone scrubbing. Dissolution rate is also a function of particle size for large-grained carbonate rocks. Fine grinding of such rocks will increase the dissolution rate to that of a fine-grained rock. Hence the requirement of high dissolution rates may be met by some grinding of fine-grained material (e.g., marl, chalk, or other limestone) or by fine-grinding coarser grained material.

For desulfurizing-fluid beds, chalks have the best capacity to absorb both SO_2 and H_2S . However, most chalks are probably unsuitable for fluidized beds because of high attrition rates. Because dolomites are generally more reactive with both SO_2 and H_2S than calcites, a dolomite would be the choice feed material for a desulfurizing-fluid bed. Other requirements are that the carbonate rock have little feldspar and few intragranular optical defects. In some applications the half-calcined dolomite would be the most reactive and, hence, the preferred feed material.

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LAKE MARLS, CHALKS, AND OTHER CARBONATE ROCKS WITH HIGH DISSOLUTION RATES IN SO₂-SCRUBBING LIQUORS*

by

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ABSTRACT

Petrographic properties of carbonate rocks are useful guides to the utilization of these rocks in SO₂-scrubbing systems. High porosity and fineness of grain are thought to be the principal properties that contribute to high dissolution rates of the rocks in the scrubbing liquor. Lake marls and chalks are the major types of carbonate rocks that have these properties. Lake marls are composed mainly of equant grains of calcite (mean grain size generally less than 4 microns) weakly agglomerated into larger, porous particles. The marls commonly consist of 80 to 90 percent CaCO₃ as calcite and aragonite. Impurities are, for the most part, quartz silt and organic matter. The average pore volume for samples of lake marls (1- to 1.2-mm particles) is about 0.50 cc/g, which corresponds to a porosity of about 57 percent. The mean size of pores in these marls is generally between 1 and 2 microns in diameter. Surface areas of lake marls range from 0.8 to 6.8 m²/g. Chalks have grain sizes and shapes similar to those of lake marls, but they generally have smaller amounts of quartz and organic matter and minor amounts of clay minerals. Pore volumes differ from one chalk formation to another; the 1- to 1.2-mm particles average about 0.20 cc/g, which corresponds to a porosity of about 35 percent. The mean diameter of pores in chalks tested ranges from 0.15 to 0.76 micron. Surface areas of chalks range from 3.2 to 20.1 m²/g.

In the United States lake marls are restricted largely to Pleistocene-age sediments that occur in the states around the Great Lakes. Chalk and chalky limestones are restricted mainly to the Upper Cretaceous and Tertiary strata in the Kansas-Nebraska-Colorado area and in the southeastern states, from Texas to Florida.

Results of laboratory tests of the relative dissolution rates of samples at pH 6 and 44°C indicate that, in addition to many lake marls and chalks, oolitic aragonite, pelecypod shells, and carbonate waste sludges from certain industrial plants also have high dissolution rates.

INTRODUCTION

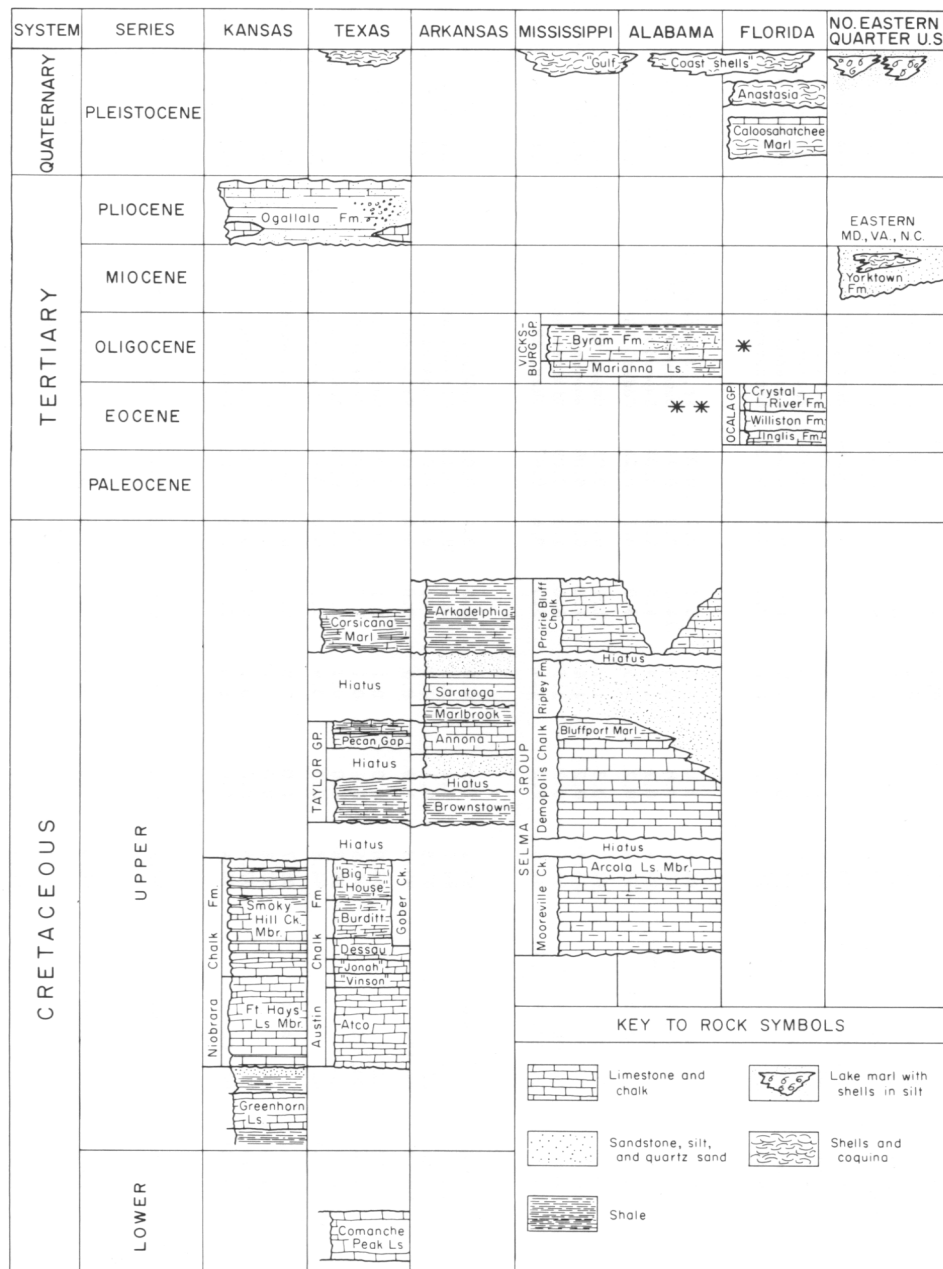
The reduction of SO₂ in flue-gas emissions from industrial and electric utility plants is a

*A major part of the work reported here was done pursuant to Contract Number 68-02-0212 with the U. S. Environmental Protection Agency.

goal shared by all persons concerned about air pollution. Disagreements arise when a decision must be made about how much reduction should be required and what is the most efficient method or process to achieve the desired reduction. This paper concerns the latter aspect of the problem and deals specifically with the question of what is the most efficient type of carbonate rock to

deposits of shells, and 1 calcitic waste sludge deposit from an industrial plant. Detailed petrographic and chemical studies were made of these samples and their calcines (the quicklimes made from the samples). The stratigraphic classification of all the deposits studied is shown diagrammatically in figure 2. In this figure the column

under each state shows formations from which samples were collected. In the areas where these formations occur, formations of other rock types and ages also are present, but are not shown here. The present report summarizes the findings of the earlier study and gives new results of SO₂-reactivity tests on 10 lake marls and 8 chalks thought



* The Marianna Limestone and the overlying Suwannee Limestone, both Oligocene in age, occur in the Florida panhandle and are in many places high-purity fine-grained porous and chalky limestones (Reves, 1961).

* * The Ocala Limestone of southeastern Alabama (and southwestern Georgia) is composed of chalky and porous limestones very similar in character to the limestones of the Ocala in Florida.

FIGURE 2. - Geologic time-rock classification of carbonate rocks studied, excluding Paleozoic limestones from Illinois. Vertical scale does not represent true thickness of rocks or duration of time.

TABLE 1. - Mineralogy, chemistry, and source of samples

Sample	Mineralogy*		Chemical analyses**						Location (nearest town)	Geologic unit
	Minor	Trace	CaCO ₃	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O		
LAKE MARLS										
7126A	AR, QZ	none	88.2	1.4	1.1	2.5	0.8	0.051	New Madison, OH	Pleistocene
7132D	none	PY	92.3	tr†	0.3	1.2	0.1	0.027	Churchville, NY	Pleistocene
7138	none	QZ, AR	91.6	1.2	0.2	0.4	0.4	0.023	Athens, IN	Pleistocene
7140	none	QZ	90.8	1.4	0.1	0.9	0.3	0.025	Kimmell, IN	Pleistocene
7150	QZ	DO, FS	83.2	1.2	0.8	8.0	0.5	0.054	Vicksburg, MI	Pleistocene
7158	none	QZ, AR	80.1	3.1	0.7	6.4	0.7	0.164	Remer, MN	Pleistocene
7162C	none	DO	85.8	1.1	0.4	3.4	0.9	0.046	Strawn, IL	Pleistocene
7163B	AR, QZ	DO	79.8	1.1	1.0	6.7	1.1	0.130	Batavia, IL	Pleistocene
7133	none	PY	91.9	0.5	0.5	1.6	0.2	0.041	Caledonia, NY	Pleistocene
7149A	none	QZ	93.2	1.7	0.2	0.4	0.1	0.030	Monterey, MI	Pleistocene
CHALKS										
7201	CL	PY, MI	84.5	2.0	1.8	6.5	0.7	0.08	St. Stephens, AL	Marianna Ls. (Tert.)
7202	CL	QZ, FS, PY, MI	70.8	0.8	5.3	14.2	2.0	0.14	Demopolis, AL	Demopolis Ck. (Cret.)
7208C	none	CL, QZ, PY, FS	89.9	0.2	1.9	4.8	1.0	0.07	Superior, NB	Niobrara Ck. (Cret.)
7212A	none	CL, QZ, FS	93.4	0.2	0.5	3.0	0.7	0.06	Cedar, KS	Niobrara Ck. (Cret.)
7213	none	CL, QZ, FS	92.7	0.3	1.2	1.9	0.4	0.05	Hays, KS	Niobrara Ck. (Cret.)
7221A	CL	QZ, FS	86.1	0.2	1.4	7.6	0.9	0.06	Woodway, TX	Austin Ck. (Cret.)
7222B	none	QZ, CL, FS	85.6	0.3	1.7	6.6	1.3	0.09	Midlothian, TX	Austin Ck. (Cret.)
7227B	CL	QZ, FS, MI, PY	87.5	0.2	1.4	5.5	0.6	0.07	Okay, AR	Annona Ck. (Cret.)
LIMESTONES										
7120	none	none	99.1	tr†	0.0	0.0	0.4	0.01	Newberry, FL	Crystal River Fm. (Tert.)
7210B	CL	QZ, FS	89.9	0.1	1.4	3.4	0.4	0.10	Gilead, NB	Greenhorn Ls. (Cret.)
7252	none	DO	97.5	0.1	0.3	tr†	0.1	0.04	Jonesboro, IL	Ullin Ls. (Miss.)
T3	DO (8)	QZ (?)	95.3	1.9	0.0	0.0	0.2	0.015	Valmeyer, IL	Kimmswick Ls. Subgroup (Ord.)
7256	DO (5)	QZ	96.0	0.3	0.1	1.1	tr†	0.02	Quincy, IL	Burlington Ls. (Miss.)
7251	none	DO, QZ	95.5	0.1	0.1	1.0	0.2	0.02	Cave-In-Rock, IL	Ste. Genevieve Ls. (Miss.)
7253	DO (16)	QZ	89.8	4.0	0.1	1.2	0.1	0.02	Anna, IL	Ste. Genevieve Ls. (Miss.)
7254	DO (4)	QZ	94.8	0.5	0.9	1.3	0.0	0.01	Prairie du Rocher, IL	Salem Ls. (Miss.)
7260A	DP (5)	none	96.7	1.0	0.0	0.0	0.1	----‡	Ste. Genevieve, MO	Salem Ls. (Miss.)
T4	none	QZ	97.8	0.0	tr†	1.5	0.3	0.047	Milan, IL	Wapsipinicon Ls. (Dev.)
65-1	none	CL	97.6	0.0	0.1	0.0	0.8	0.03	Fairmount, IL	Millersville Ls. M. (Pa.)
1363	DO (3)	QZ, CL	94.4	0.6	1.5	2.0	0.5	0.01	Casey, IL	Millersville Ls. M. (Pa.)
CALCITE SPAR										
T2	none	none	99.1	0.0	tr†	0.0	0.2	0.015	Rosiclare, IL	-----
OOLITIC SAND										
T8	none	none	98.5	0.0	0.3	0.2	0.0	0.53	Bimini Isl.	Pleistocene
SHELL										
7124	none	CL	96.4	0.1	0.0	0.9	0.1	0.34	L. Pontchartrain, LA	Pleistocene
7125	none	QZ, CL	96.2	0.1	0.3	0.4	0.5	0.41	Mobile Bay, AL	Pleistocene
7203D	AR	QZ	87.6	0.2	0.0	7.3	1.6	0.43	Chuckatuck, VA	Yorktown Fm. (Tert.)
WASTE SLUDGE										
7153	none	none	96.0	0.5	tr†	0.0	0.2	0.85	Nekoosa, WI	-----

* Major mineral component is calcite in all samples except T8 and 7124, which are both mostly aragonite. Minor = 1% to 20%, trace = < 1%. Symbols: AR, aragonite; DO, dolomite; CL, clay minerals; QZ, quartz; FS, feldspar; MI, mica; PY, pyrite. Numbers in parentheses indicate the percentage of the mineral determined by calculation of chemical analyses data.

** Weight percent, moisture-free basis.

† tr = trace amount.

‡ Not determined.

to be representative of these types; further, shells, waste sludge, and several common types of Paleozoic limestones were selected for this study (table 1). The locations of the deposits sampled for the present study are shown also on figure 1.

EXPERIMENTAL METHODS

Pore-volume and surface-area measurements

The pore-volume distribution of the samples was measured by mercury porosimetry. A maximum pressure of 15,000 psi was applied to the mercury; this pressure is sufficient to force the mercury into pores as small as 0.012 micron in diameter. Representative crushed particles, 1 to 1.2 mm in size (16 by 18 mesh), were tested.

Surface area measurements were made, in a manner described by Thomas and Frost (1971), by using a thermal conductivity cell to monitor the nitrogen adsorption and desorption curves on samples. This procedure was used to determine the surface area from a single adsorption point for the calcined samples and from multiple adsorption points for the rock samples.

The conditions of calcination, i. e., temperature, time, and partial pressure of CO₂, are highly important variables that affect the surface area and pore-volume properties of calcines (quicklimes) of the carbonate materials. Highly reactive calcines were produced by calcining samples, crushed to 1- to 1.2-mm particles, at 850°C under a nitrogen flow rate of 100 cc/min. This provided a very low CO₂ partial pressure. The time of calcination was very rapid, less than 14 minutes. The details of these experimental methods and the procedures used are given in Harvey, Frost, and Thomas (1973).

SO₂-reactivity index test method

The SO₂-reactivity test was based on the time required for the pH of a slurry containing the carbonate sample (0.5 g in 200 cc water) at about 44°C (111°F) to decrease from 6.0 to 5.8 while a nitrogen gas stream containing about 5,000 ppm SO₂ was bubbled through the slurry at about 500 cc/min. The sample was pulverized to less than 44 microns (<325 mesh). A schematic diagram of the test apparatus is shown in figure 3. Sample 7208C was used as a reference material to obtain a relative-reactivity index scale (time for sample X/time for sample 7208C). This approach for a reactivity test was taken because these test conditions are thought to more closely approximate the conditions in actual scrubbing systems than does the

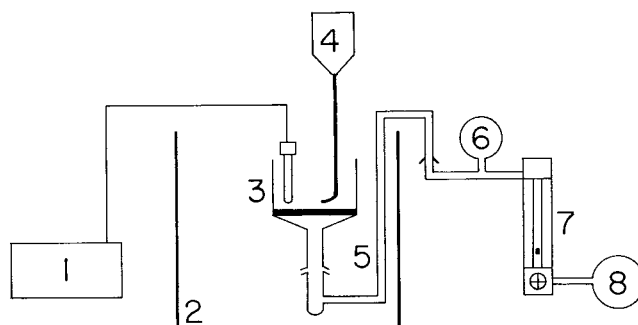


FIGURE 3. - Diagram of SO₂-reactivity test apparatus: 1, digital pH meter; 2, constant-temperature bath; 3, pyrex 350-cc medium-fritted Buchner funnel cell; 4, stirring motor; 5, pyrex glass delivery tube joined to funnel with 18/9 ball and socket joints; 6, pressure gauge; 7, rotometer flow meter and needle valve; 8, gas cylinder with about 5,000 ppm SO₂ with nitrogen balance.

measurement of dissolution rates of particles of a narrower and coarser size range at constant pH. Also, the relative-reactivity index scale eliminates the need to know exact values of the controllable variables (gas-flow rate and possibly the stirring rate) affecting the time for the pH change as long as these variables are held reasonably constant. However, even though the controllable variables were apparently held constant, some variables (partial plugging of the glass frits in the cell with use and/or changes in the SO₂ concentration supplied from the gas cylinder) could not be precisely controlled. Therefore, sample 7208C was tested repeatedly between tests of the other samples so that the observed reference time could be adjusted if these noncontrollable variables were to change.

The test procedure is as follows: The SO₂-nitrogen gas stream is made to flow through the cell just prior to the introduction to the cell of 200 cc of water preheated to about 50°C. The pH of the water is allowed to drop to about 3 before the 0.5-g sample is added. The pH of the slurry increases to about 7 and then slowly decreases as long as more SO₂ goes into solution than is neutralized by dissolution of the sample. The time required for the pH to decrease from 6.0 to 5.8 is measured. Several cells were used to obtain the tests results; the cells were back-flushed with dilute hydrochloric acid, rinsed thoroughly with distilled water, and dried before reuse.

It is assumed that the higher the rate of dissolution of the carbonate material in our simulated scrubbing liquor, the higher the reactivity that the samples would have in a full-sized wet-scrubbing system. At the present time we have no way to verify the correctness of this assumption. How-

ever, we think that it is a reasonable assumption and that the relative values obtained here will prove to be useful.

THEORETICAL REMARKS ON DISSOLUTION RATE

The rate of dissolution of calcite or aragonite crystals in a surrounding aqueous solution depends primarily on the pH of the solution and to a lesser extent on the specific chemical activity of the crystal surfaces. Calcite is slightly less soluble than aragonite. In addition, the activities of calcite and aragonite surfaces vary theoretically according to their crystallographic orientation because both minerals are anisotropic. Calcite has been observed to dissolve at much different rates depending on the orientation of the crystal surface with respect to the *c* axis (Rodgers, 1940). The activity will even vary from one specimen to another of the same mineral species if one specimen has a much higher density of crystalline imperfections (dislocations, lattice vacancies, and interstitial impurities) than the other. These imperfections tend to promote dissolution.

The rate of dissolution is affected dominantly by kinetic factors regarding the effective surface area and the actual concentration of the solute in the layer of solution adjacent to the surface. The effective surface area is not necessarily equal to the surface area as measured by gas adsorption, for some of the internal surface may not be accessible to molecules of the solvent; moreover, the proportion of the surface which is accessible normally changes as the reaction proceeds. The concentration of the solute adjacent to the surface of the dissolving solid is partly dependent on the configuration of the pores within the material and on the agitation of the solvent, because both affect the movement of the dissolved ions away from the surface of the solid.

The effective surface area of crushed materials is proportional to the size, roughness, and pore characteristics of the particles. The finer the particle size, the greater the effective surface area. The roughness of the particles is due in large part to the size of the grains making up the particles, but is due also to the nature of the fracture surface and the pores. The pores are important, independent of the roughness, in terms of the porosity or pore volume, the size distribution of the pores, and whether the pores are interconnected or isolated (permeability). In general, as the grain size decreases, as the porosity increases, as the size of the pores de-

creases, and as the permeability increases, the greater is the effective surface area. However, the fracture surface of carbonate rocks appears to be rougher for some types that have a mixture of fine and coarse grains than for those that are uniformly fine grained, and the pores must not be so small that the solvent cannot move in and out.

RESULTS AND DISCUSSIONS

Mineralogical and chemical analyses of the samples are given in table 1. In table 2 the grain size, pore volume, mean size of pores, and surface area for the rock samples, and the pore volume and surface area for their calcines are listed. The mean grain (crystallite) size was taken to be equivalent to the mean chord length of a very large number of grains as measured by image analysis (Harvey and Steinmetz, 1971). Distribution of the sizes of the grains is described as unimodal (more or less normal distribution of grain sizes) or bimodal (mixed distribution). The latter is characterized by a wide range of grain sizes and irregular or multiple modes of size of grains. The determination of the modes was made by visual examination of thin sections of the samples.

Petrography

Lake marls.—The term "lake marl" is used here as a petrographic term to describe a carbonate rock that is very soft and incoherent, is very fine grained, is composed largely of calcite, and occurs only in some freshwater lakes and bogs. Some lake marls have a pronounced sandy texture owing to the presence of abundant tubular calcitic particles $\frac{1}{4}$ to 1 mm in diameter and 1 to 10 mm long. These particles are fairly coherent; where they are very abundant, the rock is called a tufaceous lake marl.

The basins of the lakes in which marl occurs may be small, occupying only a few acres, or may be as large as several hundreds of acres. Most deposits that are at present being mined are of the order of 50 to 100 acres in extent and 10 to 30 feet thick. Current production is small compared with that of most limestone quarries and small compared with what could be produced, given a large market. Most lake marl is mined by dredging a channel through the deposit and stockpiling the marl along the bank, allowing the water to drain.

Lake marl deposits occur in the United States mainly in the glaciated areas around the Great Lakes (fig. 1). The deposits are all Pleistocene

TABLE 2. - Physical properties of samples

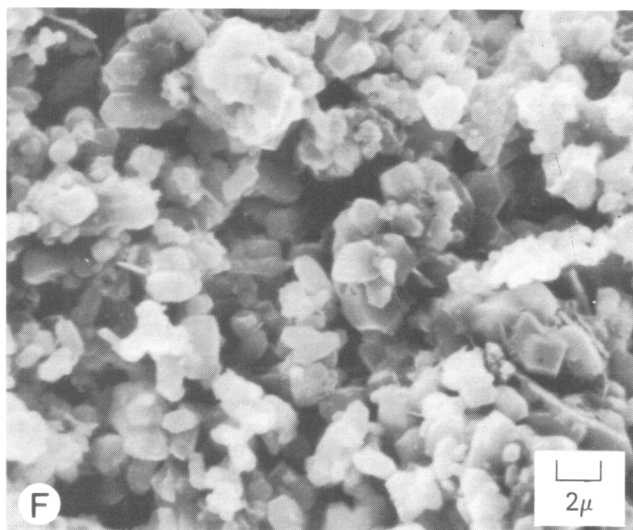
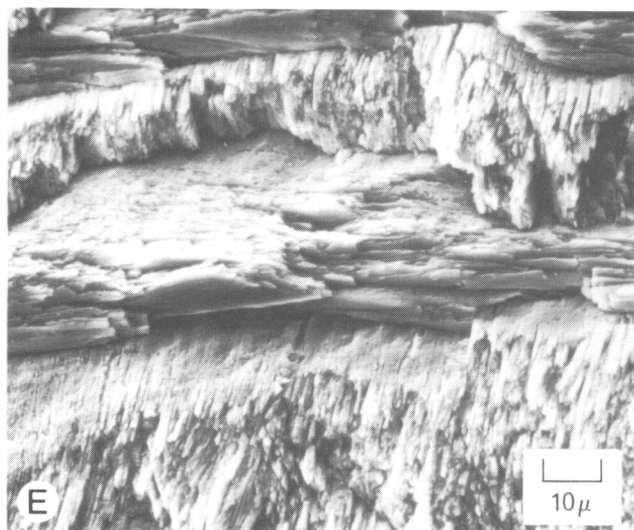
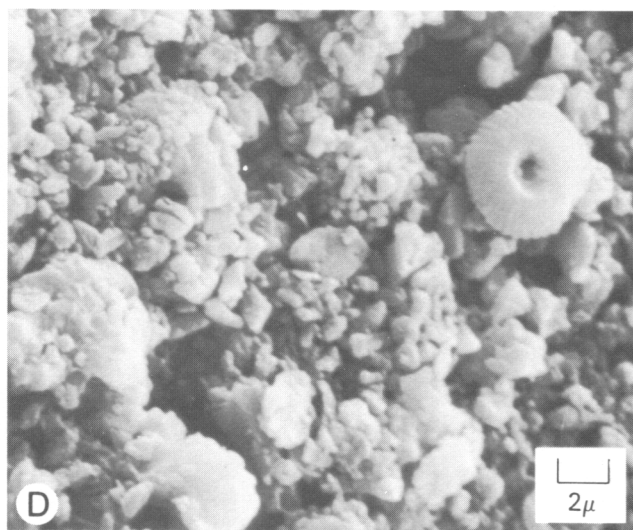
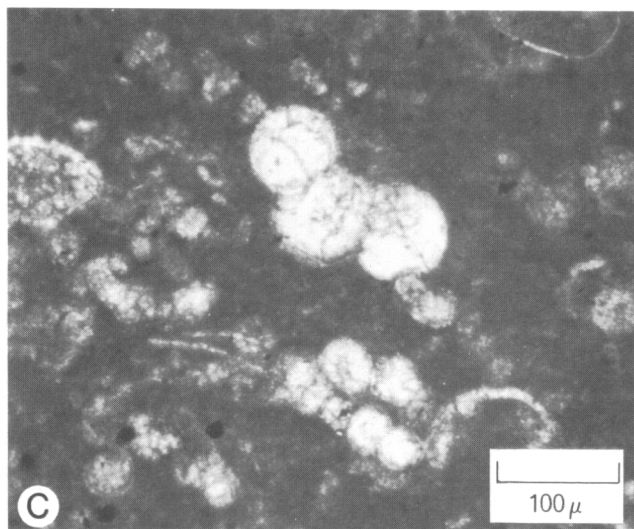
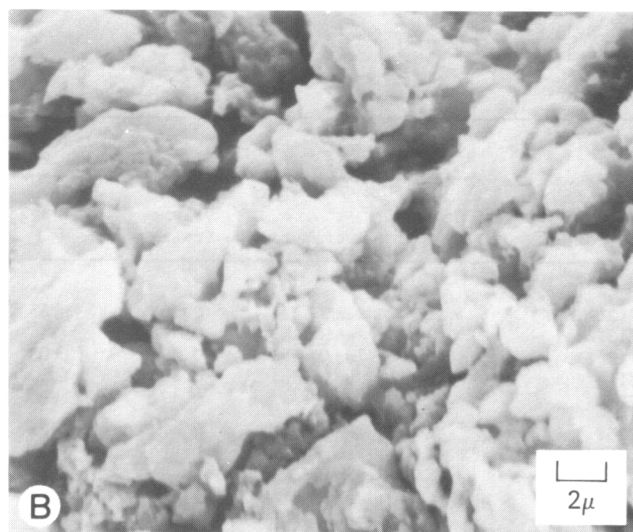
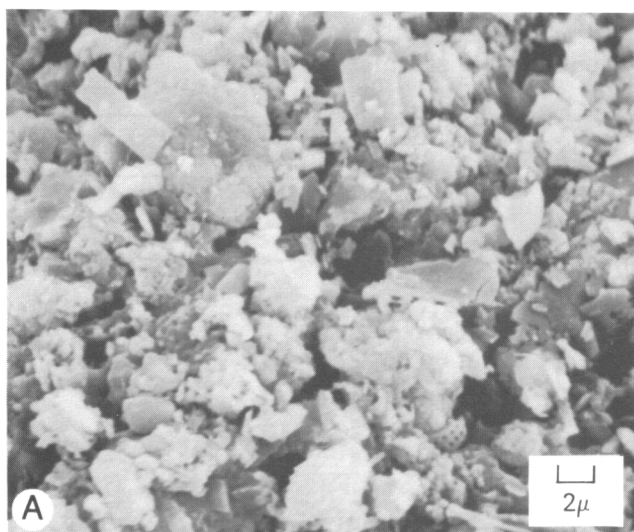
Sample	Grain size		Rock particles (1 to 1.2 mm)			Calcine (1- to 1.2- mm particles)		Rock particles (less than 44 (μ))	
	Mean (μ)	Distribution	Pore volume (cm ³ /g)	Mean pore size (μ)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Surface area (m ² /g)	Surface area (m ² /g)	SO ₂ - reactivity index
LAKE MARLS									
7126A	3.8	unimodal	0.233	1.65	—*	—*	25.2**	3.3	0.64
7132D	3.1	unimodal	0.380	0.86	3.8	1.222	21.0	2.8	0.82
7138	2.4	unimodal	0.544	1.28	4.4	1.444	20.4	3.9	0.77
7140	3.2	unimodal	0.484	1.34	2.7	1.326	26.4	2.1	0.70
7150	4.4	unimodal	0.472	1.30	3.9	0.924	22.0	2.3	0.76
7158	2.4	unimodal	0.504	1.02	5.2	1.312	26.8	4.2	0.78
7162C	4.0	unimodal	0.934	3.1	6.8	1.868	24.8	4.2	0.85
7163B	4.0	unimodal	—	—	—	—	—	4.8	0.77
7133	4.1	unimodal	0.315	4.44	0.8	0.990	15.1	1.5	0.70
7149A	2.8	unimodal	0.410	4.85	2.1	1.036	28.3	2.2	0.81
CHALKS									
7201	2.9	bimodal	0.302	0.76	8.8	0.729	24.1	3.6	0.91
7202	2.1	bimodal	0.212	0.15	17.6	0.547	13.5	10.4	1.18
7208C	2.6	bimodal	0.216	0.35	7.0	0.593	15.4	8.0	1.00
7212A	2.6	bimodal	0.217	0.39	—	0.638	15.0	3.4	1.04
7213	3.4	bimodal	0.183	0.47	4.7	0.686	16.5	2.7	0.93
7221A	2.8	bimodal	0.132	0.20	10.8	0.477	16.8	5.7	1.00
7222B	2.4	bimodal	0.152	0.18	—	0.505	11.4	6.2	0.92
7227B	3.0	bimodal	0.121	0.20	8.0	0.502	10.8	5.2	1.13
LIMESTONES									
7120	4	bimodal	0.086	0.50	.50	0.467	26.6**	1.5	0.98
7210B	4	bimodal	0.107	0.24	4.4	0.498	17.1	3.1	1.00
7252	10	bimodal	0.053	0.7	—	—	—	1.0	1.05
T3	25	mixed	0.017	0.8	—	—	34.5	0.5	0.78
7256	25	mixed	0.030	0.6	—	—	—	0.85	0.80
7251	8	mixed	0.04 †	0.3†	—	—	—	1.1	0.76
7253	8	mixed	0.038	0.3	—	—	—	1.3	0.77
7254	8	mixed	—	—	—	—	—	1.3	0.76
7260A	8	mixed	—	—	—	—	—	1.2	0.89
T4	3	unimodal	0.004	0.4	—	—	25.0	0.9	0.65
65-1	6	bimodal	—	—	—	—	—	1.5	0.56
1363	6	bimodal	—	—	—	—	—	2.1	0.55
CALCITE SPAR									
T2	1000	unimodal	0.004	< 0.1	—	—	24.1	0.6	0.57
OOLITIC SAND									
T8	2	unimodal	—	—	—	—	—	3.0	1.3‡
SHELL									
7124	1	unimodal	0.014	0.15	—	0.394	0.6	3.4	1.3‡
7125	1	unimodal	0.023	0.15	—	0.429	0.6	—	1.3‡
7203D	1	unimodal	0.039	0.56	—	0.410	0.9	2.9	1.12
WASTE SLUDGE									
7153	1.5	unimodal	0.270	0.15	—	—	0.85**	2.1	1.3‡

* Dash (—) indicates not determined.

** Particles tested were 74 to 88 μ in size.

† Estimate, based on another sample from the same geologic rock type and strata.

‡ Estimate; index is definitely greater than 1.2.



in age. In some present-day lakes, marl appears to be forming today (Terlecky, 1974).

Lake marls commonly contain organic remains of plants and scattered mollusk shells, the latter composed of aragonite. Lenticular stratification occurs by changes in the abundance of shells and by thin interlaminae of dark-colored (organic) and light-colored marl material.

The major inorganic impurities in lake marls (table 1) are quartz as partly rounded grains of silt, 4 to 30 microns in diameter, and a few similar-sized grains of feldspar. These impurities are scattered throughout the material rather than concentrated in certain layers. In some samples studied, clay and pyrite are trace constituents. Aragonite is present in some samples in amounts of as much as 10 percent because of the abundance of mollusk shells. In many marls dolomite is present in trace amounts as individual rhombs less than 10 microns across.

Electron micrographs of lake marls (fig. 4A, B) show that the marls consist of more or less equant subhedral grains of calcite weakly agglomerated into porous particles. The grains themselves range in size mainly from about 0.1 to about 4 microns. A small percentage of grains ranges up to about 15 microns across. The mean grain size of all marls tested is about 3 microns. The range of grain sizes in lake marls is small—about the same as that of sublithographic limestones—compared with that of most other types of carbonate rock materials.

Chemical analyses of lake marls sampled from active and discontinued pits show CaCO₃ values ranging mainly from 83 to 93 percent (table 1). Magnesia (MgO) content is generally 1 to 2 percent, mostly in dolomite and possibly in some clays. Alumina (Al₂O₃) content is commonly 1 percent or less; most alumina occurs in feldspar grains. Thus the clay mineral content of lake marls is remarkably low, probably less than 0.5 percent. Soda (Na₂O) content is

generally less than 0.15 percent; soda probably occurs in soluble salt crystallites or in feldspar grains and in the clay mineral impurities. The difference between 100 percent and the total of the oxides reported for the marls in table 1 is mostly the organic carbon content. This value ranges mainly from 1 to 6 percent, but one sample—a very peaty marl—tested in our previous study has more than 13 percent.

The pore volume of lake marls ranges from 0.21 to 1.08 cc/g. Representative values are shown in table 2. Pore-volume distribution curves of lake marls are shown in figure 5. The pore-volume distribution curves of the calcines of many lake marls commonly show enlargement of pores over those of the marl material in the size range larger than 0.1-micron pore diameter (samples 7132D and 7133 in fig. 5). Some calcines of marl samples show a pore-size distribution nearly identical with that of the marl throughout this range (sample 7162C, fig. 5). The large number of pores in the size range less than 0.1 micron in diameter in the calcines is due to the creation of new pores within the original grains of calcite during calcination of the marl. Some particle shrinkage apparently occurs on calcination, as the observed increase in pore volume after calcination is generally somewhat less than the theoretical increase, which is based on calculations of the data in table 2 and the CaCO₃ content of the samples. However, this shrinkage is negligible for the marls and chalks examined in this study.

The mean diameter of the pores in lake marls ranges generally from about 0.9 to 3.1 microns, and remains about the same in the calcined marls because of enlargement of the larger pores in the marl and the formation of a large number of very fine pores (<0.1 micron) during calcination. The mean diameter of these fine pores is about 0.04 micron. Thus the distribution of the size of pores is distinctly bimodal in the calcines.

The surface area of the lake marls (excluding

FIGURE 4. - Textural characteristics of some highly reactive samples. All photographs are scanning electron micrographs except C, which is a transmitted light micrograph. A, Subhedral grains of calcite 0.5 to 7 microns in diameter, loosely agglomerated in a lake marl, with a few broken pieces of diatoms (lace network) and an organic fragment (smooth, near center) scattered in the marl; sample 7163C. B, Detail of calcite grains and particles in a lake marl. C, Typical texture of chalks: sparry calcite (coarse-grained highlighted portions) in foraminifera tests surrounded by very fine calcite (dark) grains; traces of clay and magnetite (opaque) occur with the fine grains of calcite; sample 7208C. D, Detail of the very fine grains of calcite in chalk showing a coccolith and typical porous texture of the material; sample 7202. E, Interlaminated structure (cross-laminated in this case) of fibrous to bladed crystallites of aragonite on a fractured surface of a clam (*Rangia*) shell; sample 7124. F, Grains of precipitated calcite from an industrial waste sludge disposal lagoon; sample 7153.

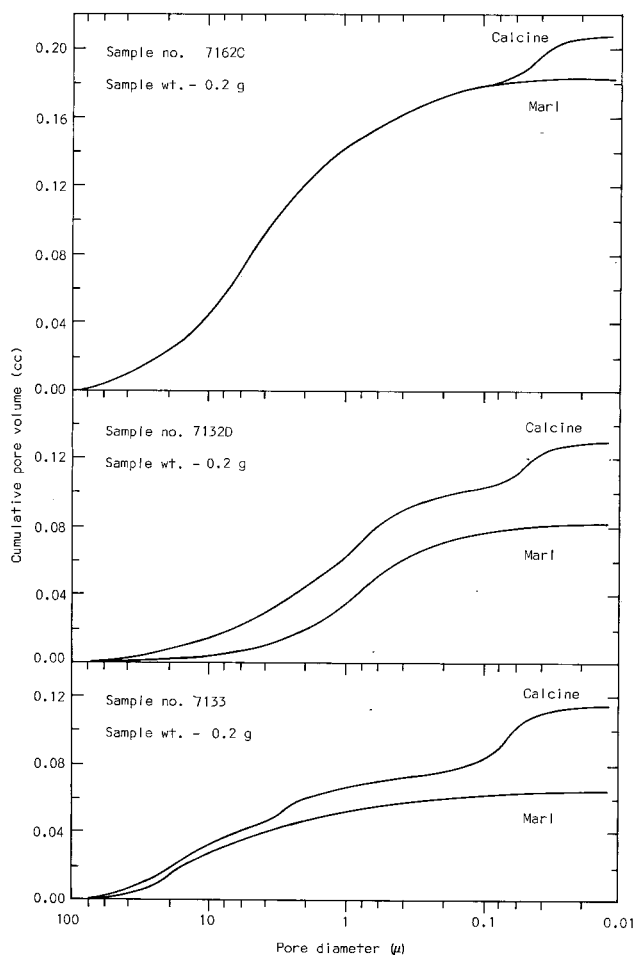


FIGURE 5. - Typical pore-volume distribution curves for lake marls and their calcines; 1- to 1.2-mm particles tested. Sample 7133 is a tufaceous lake marl.

tufaceous ones) is mainly in the range from 2.7 to 6.8 m^2/g marl; surface area of the calcines ranges mainly from 20.4 to 26.8 m^2/g calcine. In terms of the marl, this usage represents an increase of surface area upon calcination of from 5.9 to 13.6 m^2/g marl.

Chalks. —Chalk occurs principally in the Niobrara Chalk of Kansas and Nebraska and adjacent states, the Austin Chalk in central and northeastern Texas, the Annona Chalk in southwestern Arkansas, and the Demopolis Chalk (Selma Group) in Alabama and Mississippi (fig. 1). Each of these units is Upper Cretaceous in age (fig. 2). A high proportion of the commercial production of chalk from these formations is used as raw material for cement manufacture. Some chalks and chalky limestones occur in Tertiary strata—especially in the Marianna Limestone in Alabama and in the Ocala Group in Flor-

ida and Georgia (fig. 2). Also, the Harrodsburg Member of the Ullin Limestone (Mississippian) in southern Illinois contains a thick unit of chalky limestone (sample 7252, tables 1 and 2).

Chalks are composed primarily of micritic calcite (grains <4 microns in diameter), but all samples studied contain more than 5 percent of sparry calcite (clear grains >10 microns diameter) in the form of foraminifera tests (fig. 4C) scattered throughout the micrite. The average sparry calcite content of the chalks studied is 10 percent. The mean grain diameter of chalk material ranges from 2.1 to 3.4 microns. The very fine grains of calcite in chalks are broken pieces of fossil coccoliths (fig. 4D). Grain-size distribution is bimodal; the sparry calcite has a grain-size mode of about 10 to 15 microns diameter; the finer and more abundant micritic calcite has a grain-size mode of nearly 1.5 microns diameter.

The calcite (CaCO_3) content of chalks has a considerable range (table 1). Minor mineral impurities are quartz as silt grains and clay as less-than-2-micron flakes. The clay is principally montmorillonite, with lesser amounts of illite (10Å, nonexpandable) and kaolinite minerals. The illite, observed microscopically, has the form of green glauconitic pellets that are scattered through the chalk material. Traces of feldspar, mica, pyrite, magnetite, and limonite are present also in nearly every sample tested.

The pore volume of chalks ranges from 0.12 to 0.30 cc/g and averages about 0.2 cc/g; these values are somewhat lower than in most marls. The mean diameter of pores in chalks has a rather narrow range, 0.2 to 0.8 micron (table 2). The small size of the pores results in chalks having relatively large surface areas, in the range of 5 to 18 m^2/g (table 2), although those samples with surface areas greater than about 9 m^2/g have these high values because of greater abundances of clay in these rocks. Representative pore-volume distribution curves of chalks and their calcines are shown in figure 6. As in the case of marls, some chalks (7208C, fig. 6) appear to experience no pore-size enlargement during calcination, whereas others show various amounts of pore enlargement.

Limestones and other carbonate materials. —Many of the limestone samples selected for study are high-calcium limestone (≥ 95 percent CaCO_3) (table 1). Samples 7120, 7210B, 7252, and 7253 are chalky limestones; 7210B contains minor amounts of clay. Several of the remaining limestones contain minor amounts of dolomite. The pore volumes of the chalky limestones range from 0.038 to 0.11 cc/g; pore volumes for the non-chalky limestones range from 0.004 to about 0.04

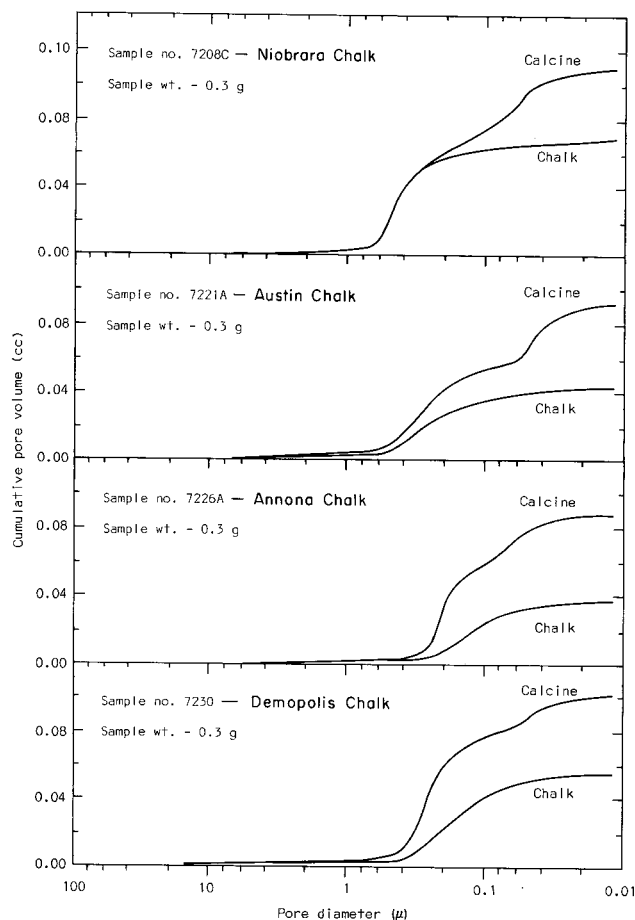


FIGURE 6. - Typical pore-volume distribution curves of chalks and their calcines; 1- to 1.2-mm particles tested.

cc/g. Representative pore-volume distribution curves are shown in figure 7: two chalky limestones (A, B), two coarse-grained crinoidal limestones (C, D), and a very fine-grained dense limestone (E).

The calcite spar sample (T2) is a vein type of calcite from a fluorspar mine in southern Illinois; the sample is very coarsely crystalline and milky colored and represents one end-member of limestone types in terms of coarseness of grain size.

Shell deposits are represented in this study by samples of the calcitic type (oysters, 7125), aragonitic type (clams, 7124), and a mixture of these two mineralogical types (7203D). The latter is a processed shell material produced from the coquina facies of the Yorktown Formation (Miocene) in Virginia. The shells all have an interlaminated structure typically represented by that shown in figure 4E. Both calcite and aragonite in the shells take the form of fibers or

blades, most of them less than 1 micron wide and 10 to 30 microns long. These are oriented parallel to one another, each with nearly identical crystallographic orientation within each lamella.

Shells typically are very dense and have small pore volumes (fig. 7F); however, calcines of shells tested have pore volumes of near 0.40 cc/g, slightly greater than the theoretical amount (0.36 cc/g) for CaCO₃. The mean diameter of the pores in calcined shells is approximately 1.5 microns.

The remaining carbonate sample, a waste sludge from a paper manufacturing plant (Nekoosa Edwards Paper Company, Port Edwards, Wisconsin), is a precipitated calcite of high purity (table 1). The trace amount of soda (Na₂O) present in this sample is relatively high compared with that in the other samples. Theoretically, soda can occur within the rapidly precipitated crystals of calcite or can occur as a soluble salt. The grain diameter of the sludge has a very narrow range and averages about 1.5 microns (fig. 4F). The sludge has a fairly high pore volume and surface

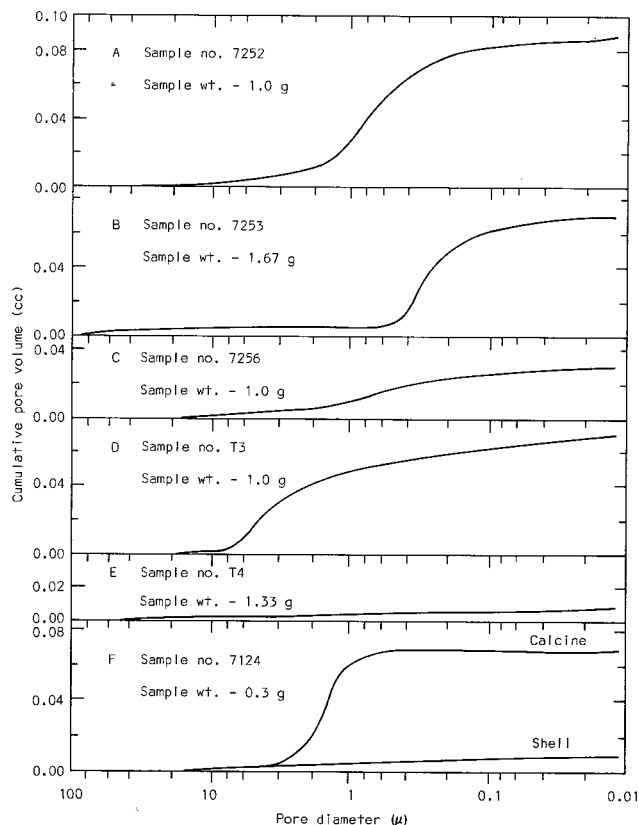


FIGURE 7. - Typical pore-volume distribution curves of: A, B, chalky limestones; C-E, limestones; and F, a shell sample and its calcine; 1- to 1.2-mm particles tested.

area compared with many of the other carbonate materials. Waste calcitic sludge from many water treatment plants and other types of industrial plants is likely to have physical properties very similar to those of this sample.

SO₂-reactivity results

The results of the laboratory tests of the relative dissolution rate of each sample, pulverized to less than 325 mesh (<44 microns), in the simulated scrubbing liquor are given in table 2. Attention should be called to the fact that four samples dissolved entirely and dissolved so rapidly in the test that no absolute index for them could be determined; however, it is our best estimate that these samples—the oolitic aragonite sand, two of the shell samples, and the waste sludge—have an index of approximately 1.3. For the purpose of this discussion, this estimate is quite adequate.

The index values range from 0.55 for one (sample 1363) of the dense fine-grained algal limestones tested to an estimated 1.3 for the samples just mentioned, more than 2.3 times the index of the least reactive sample. The other fine-grained algal limestone (65-1) tested similarly low, 0.56, and the very fine-grained limestone (T4) tested 0.65. Coarse-grained crinoidal limestones (T3 and 7256) tested 0.78 and 0.80. The chalky (porous) crinoidal limestone (7252) tested the highest, 1.05, of all the limestones.

The marls ranged from 0.64 to 0.85 and averaged 0.76; the chalks ranged from 0.91 to 1.18 and averaged 1.01. The shell samples averaged 1.24; and the oolitic aragonite and the waste sludge tested high, as discussed above.

It is difficult to predict with assurance from a study of pore-volume data, mean pore size, and surface-area measurements from gas adsorption on dry samples just what the effective surface area of a given sample will be in the reactivity test. However, consideration of these data explains to a great extent the observed reactivities of all the samples except the shells. Most limestones have relatively small pore volumes, therefore relatively small effective surface areas and consequent low reactivity indexes; this is especially true for the dense limestones. Further, lake marls have larger pore volumes than chalks, but the mean size of the pores in chalks is smaller than in marls, thus giving rise to larger surface-area values in chalks than in marls. The pores are not so tiny as to inhibit penetration by water in the reactivity test; thus the effective surface area is also larger. The relatively high reactivities of the chalks and

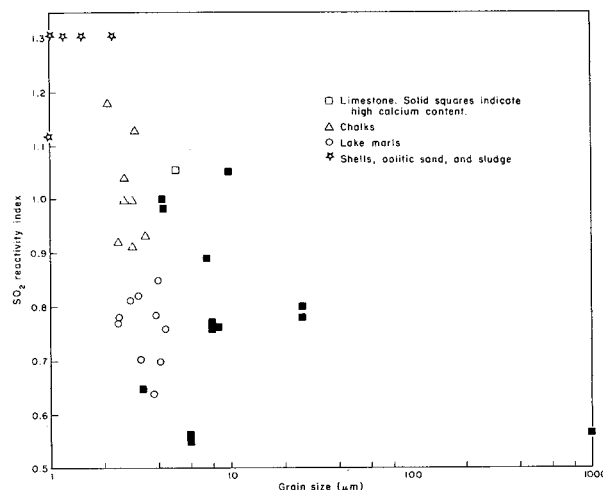


FIGURE 8. - Relation between the SO₂-reactivity index, as measured on the rock ground to less than 44 microns, and the mean grain size (crystallite size) of the rock.

marls are in agreement with these considerations.

The high reactivities found for the shells are higher than anticipated from their relatively low pore-volume and surface-area values. It is possible that the true pore volume is larger than observed, because there may be numerous pores in the shells in a size range less than 0.012 micron in diameter, the lower limit of the measurements. There also may be many isolated pores within the shells; such pores may form a closed-pore system that is not reflected in the surface-area measurements. However, neither of these possibilities is readily supported by electron microscopic analyses. Other factors may contribute to the reactivity of the shells. There is a high degree of preferred orientation of the fine crystallites in the shells. The orientation and fracture behavior of shells may be such as to expose the most reactive crystallographic surfaces of calcite and aragonite crystals to the scrubbing liquor. In addition the effect of the high soda content of the shells may be a very important factor, as discussed below.

Graphical analyses of the properties of the samples in relation to their SO₂-reactivity indexes are shown in figures 8 through 11. The grain-size graph (fig. 8) indicates a general trend of increasing index with decreasing size. The fine-grained and dense limestones have an anomalously low index according to this trend. The calcite spar, coarse-grained limestones, chalks, shells, and sludge fit this trend moderately well.

The pore-volume graph (fig. 9) shows little

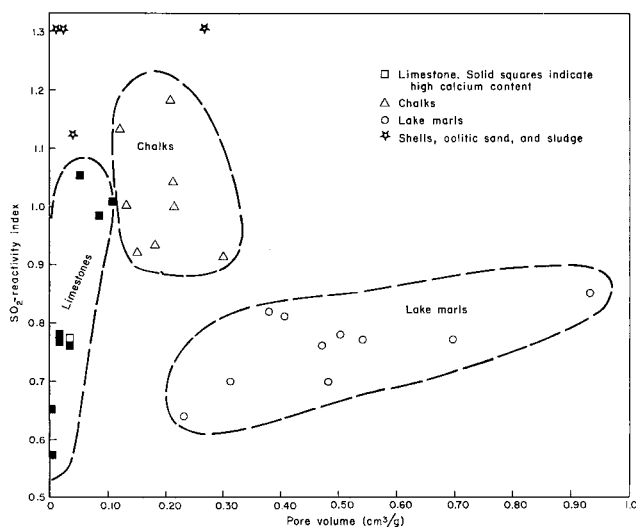


FIGURE 9. - Relation between the SO₂-reactivity index, as measured on the rock ground to less than 44 microns, and the total pore volume, as measured on 1- to 1.2-mm particles.

overall correlation, although the different rock types plot in separate areas of the graph; for the limestones and lake marls, considered apart from the others, increasing SO₂-reactivity index is accompanied by increasing pore volume. However, the rate of increase is decidedly different for these two rock types. The data of the chalks appear to show an extension of the general trend shown by the limestones. The shells,

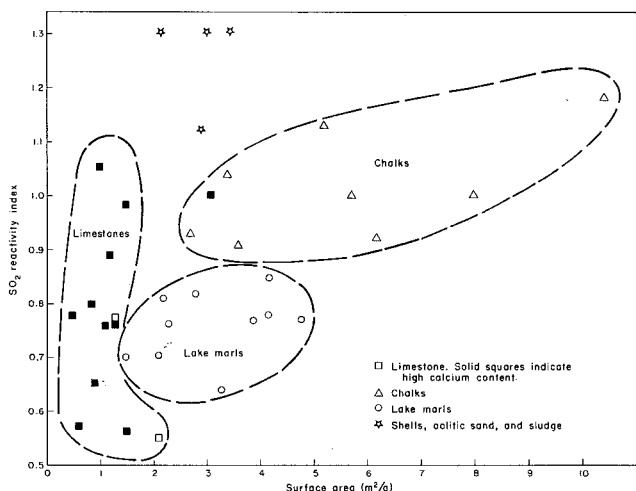


FIGURE 10. - Relation between the SO₂-reactivity index and surface area. Particles of less than 44 microns were tested for both properties.

with their very low pore volumes, are not in agreement with this trend, but the behavior of the waste sludge sample is. Lake marls have a lower reactivity than expected, considering only their high pore-volume values.

The relation of the surface area to the SO₂-reactivity index, both measured on samples pulverized to minus 325 mesh, is shown in figure 10. Some similarities exist between this graph and figure 9, but the lake marls are grouped in a random pattern; the chalk samples appear to show a trend of increasing index with increasing surface area.

The relation of the soda content, as determined analytically on the whole rock material, to the SO₂-reactivity index (fig. 11) shows a general trend of increasing index with increasing weight percentage of soda. The various types of rocks are not grouped into any distinct pattern on this graph. Other chemical results do not correlate with the reactivity index. The apparent correlation of index with soda content is not fully understood. Sodium that occurs as interstitial ions within the crystal structure of calcite and

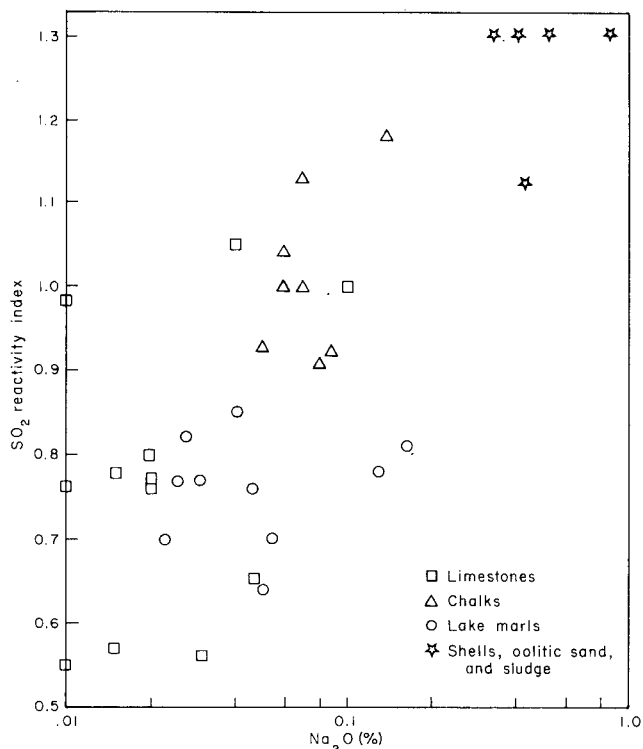


FIGURE 11. - Relation between the SO₂-reactivity index, as measured on the rock ground to less than 44 microns, and the sodium oxide content of the rock.

aragonite, or as inclusions within grains, or as a soluble salt along grain boundaries would probably act to increase reactivity. However, it is difficult to understand how other occurrences of soda in the rocks, whether in clay or in feldspar mineral impurities, would enable it to act to increase reactivity.

CONCLUSIONS

Conclusions drawn from these data indicate that pulverized shells from deposits along the coasts have good potential for high rates of dissolution in SO_2 -scrubbing liquors, as does oolitic aragonite sand. Our results show a very high rate of dissolution for a calcitic waste sludge material; this may be especially significant for certain areas in the country where limestone resources are limited and where calcitic waste

sludge is available from paper, water treatment, and other types of industrial plants. Such waste material is likely to be very reactive in wet-scrubbing systems. Chalks appear to be more reactive than most limestones, and lake marls are likely to be more reactive than dense fine-grained limestones, no matter how finely such limestones are pulverized.

Lake marl, because of the ease of its production (no blasting and little or no crushing), together with its high degree of disaggregation when mixed with water, should be given important consideration for use in limestone scrubbing systems at power plants near such deposits.

The soda (Na_2O) content and the grain size (crystallite size) of a carbonate material, as well as the pore-volume and surface-area properties, appear to be useful guides to the SO_2 -reactivity index of the material.

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IMPACT ON THE LIMESTONE INDUSTRY OF THE USE OF THROWAWAY-SCRUBBING PROCESSES BY UTILITIES

by

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ABSTRACT

The technology for using limestone or lime to scrub SO_2 from power-plant flue gas has significant implications to the limestone industry. A brief status report on these processes will be made, possible process requirements on the limestone properties will be reviewed, and projections on the buildup of demand with respect to time will be reviewed. Disposal problems inherent with the use of these throwaway processes will also be summarized. Given a viable technology, relations among (1) distance of power plants from low- and high-sulfur coal and limestone deposits, (2) modes of handling and transporting immense tonnages of bulk material—coal and/or limestone, and (3) regional air-quality standards are some of the factors which will ultimately determine the demand for limestone. A discussion of these factors will be presented, with the intent of identifying geographic regions where significant increases in production can reasonably be expected.

INTRODUCTION

The predominant energy source for U. S. power generation has always been coal. How much the total demand for coal will grow, and how fast, has always been somewhat uncertain, but in the past six months this situation has become much more confused because of many conflicting factors, principal of which are: availability of oil and gas, coal mine closings because of safety, electrical load curtailment by customer conservation, restrictions on the use of high-sulfur coal, unreliability of SO_2 -removal methods, and nuclear power trends.

Although this country has yet to establish a national energy policy and will apparently take considerable time to do so, it now seems clear that gas, our scarcest fuel, will gradually be phased out as a power source. As shown in table 1, the trend in recent years has been mostly toward an increasing percentage in the use of oil and gas. That trend will now be reversed to favor coal, at least until the growth of nuclear

power becomes significant. At the same time, most predictions show that the demand for coal in the generation of power will increase with time at least until 1990, despite all other technical developments. However, much of the expected increase in coal consumption in new utility boilers will not involve limestone or its products for SO_2 control because the new coal being used is largely low-sulfur western coal. The newest large plant, 1,300 Mw, just announced by American Electric Power, is to be built on the West Virginia side of the Ohio River near Pomeroy, Ohio, and will use only low-sulfur Wyoming coal on long-term contract. The coal will be transported to the Mississippi by unit train or pipeline and then barged up the Mississippi and Ohio Rivers to various power plants. This trend will accelerate until scrubbing systems become readily available.

All current throwaway-scrubbing systems on utility boilers require lime or limestone as the reactant. Although by-product stack-gas-recovery schemes, such as the Wellman-Lord process,

TABLE 1. - Electric utility generating plant
fuel consumption, 1962-71*

Year	Coal (short tons)	Gas (MCF)	Oil (41-gal bbl)
1971**	327,926,249	3,992,980,610	396,237,967
1970	320,818,141	3,931,996,247	335,503,752
1969	310,640,917	3,487,642,263	251,036,935
1968	297,779,069	3,147,908,961	188,641,862
1967	274,184,533	2,746,352,409	161,278,197
1966	266,476,823	2,609,948,660	140,948,854
1965	244,788,119	2,321,100,937	115,392,583
1964	225,425,457	2,332,895,816	101,140,953
1963	211,322,494	2,144,473,200	93,313,584
1962	193,238,309	1,965,973,740	85,768,011

*Dupree and West, 1972.

**Includes Alaska and Hawaii; data preliminary.

TABLE 2. - Major limestone/lime demonstration programs on boilers

Year	Plant	Source	Size
Limestone scrubbing			
1932	Battersea Power Station - London	--	165-Mw coal
1972	Commonwealth Edison - Will County	Babcock and Wilcox	156-Mw coal
1973	City of Key West - Stock Island	Zurn Industries	37-Mw oil
1973	Kansas City Power and Light - La Cygne	Babcock and Wilcox	820-Mw coal
1973	Arizona Public Service - Cholla	Research-Cottrell	115-Mw coal
1973	Detroit Edison - St. Clair	Peabody	180-Mw coal
1975	TVA - Widow's Creek	TVA	550-Mw coal
1976	Northern States Power - Sherburne County	Combustion Engineering	680-Mw coal
1977	Northern States Power - Sherburne County	Combustion Engineering	680-Mw coal
Limestone injection			
1968	Union Electric - Meramec	Combustion Engineering	140-Mw coal
1968	Kansas Power and Light - Lawrence	Combustion Engineering	125-Mw coal
1971	Kansas Power and Light - Lawrence	Combustion Engineering	400-Mw coal
1972	Kansas City Power and Light - Hawthorn	Combustion Engineering	130-Mw coal
1972	Kansas City Power and Light - Hawthorn	Combustion Engineering	130-Mw coal
Lime scrubbing			
1969	Sodersjukhuset - Stockholm	Bahco	18-Mw* coal
1972	Mitsui Aluminum - Omuta	Chemico	120-Mw* coal
1973	Louisville Gas and Electric - Paddy's Run	Combustion Engineering	65-Mw coal
1973	Duquesne Light - Phillips	Chemico	180-Mw coal
1974	Ohio Edison - Bruce Mansfield	Chemico	880-Mw coal
1975	Ohio Edison - Bruce Mansfield	Chemico	880-Mw coal
1976	Columbus and Southern Ohio - Conesville	Not selected	2 x 376-Mw coal

*Electrical equivalent.

are also prime candidates for SO_2 control, they do not generally employ lime or limestone and therefore are not of direct interest to the limestone industry.

STATUS OF TECHNOLOGY

As shown in table 2, about a dozen full-scale demonstration projects for limestone or lime scrubbing on boiler stacks have been started up in recent years; these projects have met with varying success. Limestone/lime scrubbing can be operated three ways: by injecting limestone into the power-plant boiler and catching it in a wet scrubber after the air preheater, by introducing limestone directly into the scrubber system, or by introducing lime in a similar fashion. Limestone injection into the boiler has fallen into disfavor because of operating problems such as abnormal slagging and increased erosion in the boiler and plugging in the scrubber. Plans call for the four limestone-injection demonstration plants still operating to be converted to tail-end scrubbing.

The first scrubbing process was installed on a power plant located at the Battersea Power Station in London and is termed the Battersea process. This installation and the one at the Bankside Station in London were put in in 1929 as a result of public opinion in England following a series of exceptionally severe smogs. The process is shown in figure 1. The original Battersea installation treated the effluent gas from coal with an average sulfur content of 0.9 percent in such a fashion that only 9 percent of the sulfur escaped into the atmosphere. The process is relatively simple; it took advantage of the fact that the River Thames, which supplied the water for scrubbing the flue gases, already contained most of the alkali required to neutralize the sulfur dioxide in the effluent gases. In addition, the river carried away the waste product, calcium sulfate, in solution. Thus use of the process was favored by natural conditions.

Essentially the flue gas was washed with a slurry of chalk (calcium carbonate) on grid scrubbers; only enough chalk was added to the river water to maintain the alkalinity required to neutralize the SO_2 in the effluent gases. Crude manganese sulfate was added to the effluent to activate the oxidation of sulfite in the aeration tank. The solution from the scrubber passed to a settler and into an oxidizing tank before being sent to the river. The cost of this process was in the range of 12 to 15 percent of the cost of delivered coal. Other limestone processes are shown in table 2.

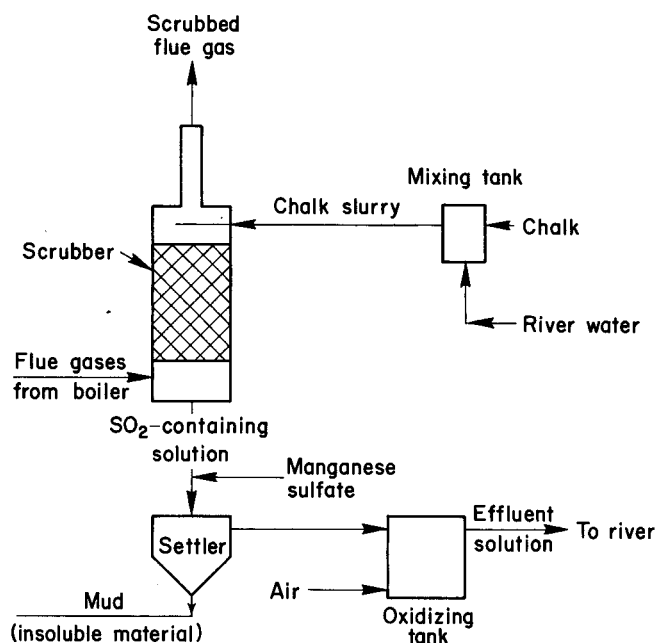


FIGURE 1. - Flow diagram of the Battersea process.

Will County Unit 1 of Commonwealth Edison was retrofitted with tail-end limestone scrubbing, and the scrubbers were started up in February 1972. The scrubbing system was purchased from Babcock and Wilcox and involves Venturi scrubbers, in series, with either a sieve plate column or a turbulent contact absorber (two parallel scrubbing modules). The major nonmechanical problems involve plugging of the demisters above the scrubbers and sometimes the scrubbers themselves. Disposal of the sludge is an unsolved problem; however, attempts are being made to stabilize the sludge by the addition of lime and fly ash. During two years of operation, the availability of the scrubbing modules has been about 25 percent for each module.

The Key West oil-fired plant built by Zurn Industries on Stock Island uses a seawater slurry of native coral and was scheduled to go on stream in July 1972; however, it was delayed by operational problems until August 1973. The system uses a Zurn absorber design which requires a stoichiometric ratio of 3.5 to achieve an SO_2 -removal efficiency of about 70 percent. Thus far the system has minimal operating experience because of problems with controlling the liquid level in the scrubber; this level is very critical for proper operation. Sludge disposal on the space-limited island is a very major unsolved problem.

The La Cygne plant of Kansas City Power and Light employs a seven-module Babcock and Wil-

cox system, similar to that of Will County; each module can operate independently of the others. This station is experiencing problems with both the generating plant and the scrubbers. First reports from Arizona Public Service's Cholla plant, where Research-Cottrell has installed a tail-end limestone-scrubbing system, indicate that the system is working. However, several more months of operating experience will have to be achieved before any definite conclusions can be reached.

By reference to table 2 it can be seen that limestone injection was pioneered by Combustion Engineering and was first practiced commercially at the Meramec Plant of Union Electric in 1968. Combustion Engineering favors the use of marble-bed absorbers. Because of special construction features of the Union Electric boilers, the plant was especially susceptible to fouling of the boiler tubes and the experiment was eventually terminated. There were also additional problems with scrubber scaling, demister operation, and waste disposal. In late 1968 the limestone-injection system on a 125-Mw unit at Lawrence was started up by Kansas Power and Light Company in a simple configuration with no slurry recycle to the scrubber. This system encountered problems with gas distribution, scrubber plugging, corrosion, and erosion. After several years of operation (mostly during the winter when coal is being fired) and many modifications the unit is still experiencing problems. In late 1970 a new 400-Mw unit was started up at Lawrence with limestone injection according to a design based on the experience with the 125-Mw unit. However, both units are still experiencing scaling problems in the scrubber; this has made it necessary to reduce the limestone feed to the boiler at the expense of lower SO_2 -removal efficiencies. The units are kept in operation by nightly cleanup of half of the scrubbers, which are taken off line when the system is at reduced load. Kansas Power and Light is going to switch both units to tail-end limestone scrubbing. Two additional limestone-injection systems went on stream in late 1972 at Kansas City Power and Light's Hawthorn Station and they have been experiencing problems similar to those at Lawrence. The point of limestone injection has been switched from the boiler to the air-preheater exit so that limestone rather than lime is now carried into the scrubber by the flue gas.

However, the most successful processes so far have all employed lime as the reactant, and these are summarized at the bottom of table 2. One of the oldest units which has worked, and is still operating, is in Sweden and is based on

lime scrubbing. The first commercial installation of this system went into operation in November 1969 at Sodersjukhuset, a large hospital in Stockholm. With the success of the first unit, two additional units were installed. However, the units are relatively small and operate on fuel oil, thereby avoiding complications induced by fly ash. The system has been licensed to Research-Cottrell in the United States, and a number of additional installations are now in operation in Japan.

The first major large-scale demonstration of lime scrubbing was the Chemico installation of the Mitsui Aluminum Company in Japan. This installation has now had well over a year of continuous operation, using carbide lime sludge as the reactant. Perturbations in power-plant operation peculiar to a utility boiler are not involved, because the Japanese facility's purpose is to generate steam at a relatively constant load; however, the plant has demonstrated long-term reliability on a fairly large scale. Although the initial claims involved closed-loop operation, this has now been discounted to some extent, and partial open-loop operation appears feasible. Demonstration of reliable closed-loop continuous operation on a coal-fired plant is, of course, the key issue in our current problem with respect to stack-gas control. Until the recent experience at Louisville, this issue remained in serious doubt.

Perhaps the most successful demonstration plant in the United States to date is the carbide-lime-scrubbing installation at Louisville Gas and Electric's Paddy's Run Station. The system was purchased from Combustion Engineering and uses marble-bed absorbers. From start-up in April 1973 through December 1973, the system had an availability of 90 percent, with the longest continuous run being 45 days. However, in order for the system to be widely applicable to other utilities, the successful use of hydrated lime rather than carbide sludge should be demonstrated. Also, the system at Paddy's Run has avoided the formidable problems of stack-gas reheat and waste disposal by using natural gas for reheat and by dumping the sludge in a borrow pit.

The first demonstration plant in the United States to use hydrated lime will be the Chemico installation at Duquesne Light's Phillips Station. The system started up in April 1973, but shut down the following October because of leakage in the stack, corrosion cracking near the welds in the induced-draft fans, and abrasion and corrosion in the scrubber vessel. The system was started up with fly-ash removal only, and the reactant lime has not yet been tried.

The experience to date with limestone/lime-

scrubbing systems for SO_2 control indicates that progress is being made with tail-end systems. However, there is still substantial disagreement between vendors, utilities, and various institutional organizations on rates of progress, the commercial availability of these processes, and the magnitude of the problems remaining to be solved. The recent official projections of the Environmental Protection Agency are used later in this review, although these figures are believed to somewhat overrate the current state of technology (Rosenberg and others, 1973).

DISPOSAL PROBLEMS

The major problem inherent in flue-gas-desulfurization systems based on lime or limestone is the necessity to dispose of or utilize large quantities of sludge. At present, lime/limestone-scrubbing systems generate a sludge with little commercial value. Lime-scrubbing processes ordinarily produce sludges containing $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 ; limestone sludges generally contain $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and CaCO_3 . For coal-fired installations where efficient particulate removal apparatus is not installed upstream of the absorber, such sludges can contain large quantities of coal ash.

The amount of sludge generated by a given plant is a function of the sulfur and ash content of the coal, the coal usage, the on-stream hours per year (load factor), the mole ratio of lime or limestone added to the amount of SO_2 removed, the SO_2 -removal efficiency, the ratio of sulfite to sulfate in the sludge, and the percent moisture in the sludge.

The SO_2 -removal efficiency will differ from one flue gas desulfurization system to the next as a function of local requirements. Typically, an SO_2 -removal efficiency of about 85 percent is required to meet the standards for plants burning eastern coal.

Because unreacted additive is disposed of with the sludge, the stoichiometry of lime or limestone addition (the CaO/SO_2 or $\text{CaCO}_3/\text{SO}_2$ mole ratios) greatly influences the amount of sludge to be handled. The CaO/SO_2 and $\text{CaCO}_3/\text{SO}_2$ mole ratios differ from system to system at present, but the general trend is toward lower values as operating experience is gained. Reasonable values for these ratios are 1.0 and 1.2, respectively.

Other factors influencing the amount of sludge to be handled are the load factor of the plant, the coal-use rate, and the mole ratio of sulfite to sulfate in the sludge. The amount of sludge pro-

duced by a plant is directly proportional to the number of hours per year that the plant operates and the coal usage of the plant. Obviously, if the plant is on line a larger fraction of the year or more coal is required per kw-hr, the amount of sludge produced will increase. The sulfite-to-sulfate ratio in the sludge also affects the weight of the sludge produced because $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is heavier than $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Table 3 shows the quantities of ash and sludge produced per year by a 1,000-Mw coal-fired station controlled by lime/limestone flue-gas desulfurization. Using the forecast for flue-gas desul-

TABLE 3. - Typical quantities of ash and sludge produced per year from a 1000-Mw coal-fired power station*

Item	Metric tons/yr
Coal ash, dry	306,000
Coal ash, wet (50% solids)	612,000
Limestone sludge, dry**	
$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	236,000
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	35,000
CaCO_3 unreacted	84,000
	355,000
Limestone sludge, wet (50% solids)	710,000
Limestone sludge, wet (with ash)	1,322,000
Lime sludge, dry**	
$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	236,000
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	35,000
CaO unreacted	20,000
	291,000
Lime sludge, wet (50% solids)	582,000
Lime sludge, wet (with ash)	1,194,000

*Assumptions:

Coal: 3.0% S; 12% ash
Plant: 6,400 hr/yr; 0.4 kg coal/kw-hr
Scrubber: 85% SO_2 removal
1.0 CaO/SO_2 (inlet) mole ratio
1.2 $\text{CaCO}_3/\text{SO}_2$ (inlet) mole ratio

**Sulfite/sulfate ratio based on performance of Chemico scrubbing unit at Mitsui Aluminum Co., Japan.

furization given in the SOCTAP report (Sulfur Oxide Control Technology Assessment Panel, 1973), the amount of wet sludge that will have to be disposed of annually by 1980 is estimated to be about 115×10^6 metric tons (127×10^6 tons). This value is based on the assumption that 116,000 Mw of generating capacity will be controlled by 1980 and that 75 percent of the control will be lime/limestone-scrubbing systems.

The solid-waste-disposal problem presented by lime/limestone-scrubber sludges can be put in perspective by comparison to other industries and activities. Phillips and Jones (1973) made such a comparison, and the state of Ohio was chosen as an example. In terms of quantity, estimated Ohio scrubber-sludge production in 1978 will present a disposal problem similar to that of municipal refuse. Because of the lower density of scrubber sludge, however, eight to ten times as much space is required for refuse disposal. In terms of weight the present disposal of phosphate rock slime and gypsum from fertilizer manufacturers in Florida presents a problem two to three times that of scrubber sludge in Ohio.

Ponding and landfilling currently provides the major mechanism for disposal of lime/limestone sludges from flue-gas desulfurization systems. There are three problems associated with this practice. First, the land use for waste disposal is esthetically objectionable. Second, the sludge could provide varying degrees of surface and ground-water pollution, depending upon chemical composition, solubilities, and location, design, and operation of the disposal site. The potential water pollution problems stemming from the chemical composition of the sludge may be classified as (1) soluble toxic species (toxic meaning elements which can cause health problems even at low concentrations), (2) chemical oxygen demand, (3) excessive total dissolved solids, (4) excessive levels of specific species, e.g., sulfate and chloride, not generally thought of as toxic, and (5) excessive suspended solids (some of which might dissolve later). Thirdly, for land reclamation, most of the stable wastes will require only a cover material to support vegetation and to prevent eventual erosion. However, some wastes are very resistant to dewatering and could reslurry in the pond or landfill. If this is shown to be true, it is likely the chemical fixation will become a necessary practice. Chemical fixation of limestone-scrubber sludge is currently being attempted at the Will County Station of Commonwealth Edison.

The alternative to disposal of scrubber sludges is development of commercially applicable utilization processes. Numerous programs

in this area have been conducted through government sponsorship and by industry (Minnick, 1974; U. S. Environmental Protection Agency, 1974). These may be summarized as follows:

1. Filler material
 - A. Structural fill
 - B. Mine-void fill
 - C. Filler in bituminous concrete
 - D. Waste-disposal/sanitary-structural landfill
2. Pozzolanic products
 - A. Road base course
3. Autoclave products
 - A. Concrete admixture (structure and products)
 - B. Fired brick
 - C. Lightweight aggregate
4. Pressure-sintered products
 - A. Metal coatings
 - B. Pipes
5. Gypsum products
 - A. Plaster
 - B. Wallboard
6. Soil amendment
7. Mineral wool
8. Mineral recovery
 - A. Lime
 - B. Aluminum
 - C. Iron
 - D. Titanium
 - E. Silicon
 - F. Rare elements
9. Sulfur extraction
 - A. Sulfur
 - B. Sulfuric acid
10. Polluted water treatment
 - A. Recovery of polluted streams, ponds, lakes
 - B. Neutralization of acid mine drainage and polluted waters
 - C. Sewage-plant treatment

Although many of the above schemes have been proposed as uses for lime/limestone-scrubber sludges, none is being currently utilized by the U. S. power industry. At present the power industry is extremely anxious to employ strategies which entirely circumvent the sludge problem: development of by-product recovery processes, coal pretreatment, or use of low-sulfur fuels.

PROJECTED NEEDS

Last fall, over a period of about a month, the Environmental Protection Agency conducted extensive hearings concerning the status and projected future of stack-gas scrubbing in the United States (U. S. Environmental Protection Agency,

1974). The official conclusions of the hearing panel with respect to commercial availability of the various flue-gas-desulfurization (FGD) processes is summarized below:

The panel finds that the following commercially available FGD process/application combination can be installed with the expectation of successful operability and reliability, in approximate order of confidence:

FGD System	Power Plant	By-Product
Wellman-Lord	Oil	Sulfuric acid
Lime scrubbing	Coal or Oil	Throwaway
Wellman-Lord	Coal	Sulfuric acid
Limestone scrubbing	Coal or Oil	Throwaway

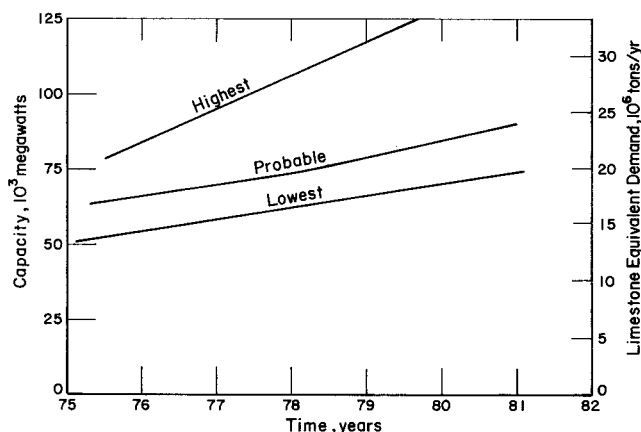


FIGURE 2. -FGD for coal-fired power plants: cumulative need (U. S. Environmental Protection Agency, 1974).

The panel's estimate of cumulative need is shown in figure 2 for three levels of confidence. The highest curve is based on pessimistic projections for new low-sulfur coal supplies and minimal redistribution of existing supplies. The lowest curve represents EPA's more optimistic projections, and the most probable curve is, of course, intermediate between these two estimates. The estimated ability of industry to supply such needs is shown in figure 3, where estimates provided by the Industrial Gas Cleaning Institute and an earlier SOCTAP report are given. Limestone-equivalent demand, assuming 25 percent excess limestone, 3 percent sulfur, 12,500 Btu/lb coal, and electrical efficiencies of 33 percent, is shown on the right-hand side of these figures.

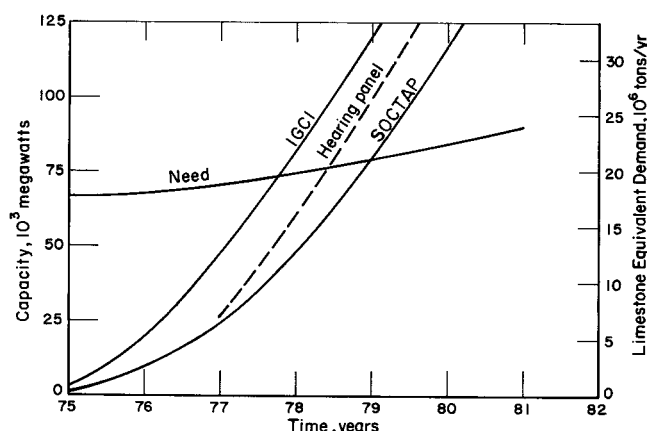


FIGURE 3. - FGD for coal-fired power plants: cumulative need and vendor capacity (U. S. Environmental Protection Agency, 1974).

AVAILABILITY OF LIMESTONE OR LIME

The use of carbonate rocks in stack-gas scrubbing now looms on the horizon. This potential use portends an annual increase in production of somewhere between 20 and 40 million tons, depending upon assumptions made and time frame of the prediction. As shown in table 4, this is only perhaps 3 to 6 percent of present production. Nevertheless, this potential use represents a substantial tonnage, and the topic of availability of the resource is receiving attention by many utilities.

TABLE 4. - Estimates of availability of limestone for flue-gas desulfurization*

Region	Millions of tons/year	
	FGD demand	Total production
New England	1.4	2.4
Middle Atlantic	6.6	90.9
East North Central	14.3	185.6
West North Central	2.7	92.5
South Atlantic	8.5	87.5
East South Central	5.6	81.3
West South Central	--	58.3
Mountain	1.4	10.7
Pacific	0.3	18.8
	40.8	628.0

*O'Donnell and Sliger, 1972.

One of the most important parameters in tail-end-scrubbing systems is the reactivity of limestone or lime available for use in such systems. The two previous papers have reviewed much of our knowledge in this area, and Drehmel's work has been reported previously (1971). There is much less known about the reactivity of lime of various compositions, and lime obtained from carbide sludge is the only lime successfully used to date in large-scale scrubber operation. The availability of carbide sludge is obviously very limited; it would be available to only a very small fraction of the power industry.

Carbonate rock high on the interest list is obviously limestone with 90 to 95 percent CaCO_3 ; environmentally, probably the less the magnesium content the better. Although United States carbonate deposits are extensive—according to one estimate 3.6×10^{12} tons as represented by surface deposits (O'Donnell and Sliger, 1972)—other estimates indicate that known reserves of high-purity limestone will be exhausted within about 50 years. It would seem that a viable technology, including scrubbing and waste disposal, will be needed to permit carbonate rocks other than high-purity limestone to be used.

It would thus appear that the only major impact, if lower purity limestone is used, would be in the New England area, where new deposits may be required or substantial transportation requirements might arise. However, the percentage of power plant needs represented by this imbalance is relatively small. Future costs for suitable limestone were estimated by O'Donnell and Sliger (1972) to be less than approximately \$4/ton, and maximum transportation costs to power plants were believed to be less than \$2/ton. By comparison the average price for limestone in the United States in 1969 was estimated to be \$1.45/ton. Should high-purity limestone be required, as opposed to just being desirable, exploration to increase proven reserves is to be expected. Whatever the purity of rock required, new quarries and mines are foreseen to minimize the distance between the carbonate deposit and, if not a single power plant, then certainly groups of power plants.

However, a much more serious problem will develop if lime is required for stack-gas control. As shown in table 5, the demand for lime by flue-gas desulfurization, using the same basis as in table 4, could be about 27 million tons per year. This compares with a total production in the United States of about 21 million tons in 1971 (Reed, 1971). Only two regions of the country,

TABLE 5. - Estimates of availability of lime for flue-gas desulfurization

Region	Millions of tons/year	
	FGD demand	Estimated production
New England	0.9	0.4
Middle Atlantic	4.4	2.4
East North Central	9.6	7.4
West North Central	1.8	1.8
South Atlantic	5.7	1.5
East South Central	3.7	1.4
West South Central	--	3.1
Mountain	0.9	2.0
Pacific	0.2	0.7
	<u>27.2</u>	<u>20.7</u>

the West South Central region and the Pacific region, would not be seriously affected by this demand. The average price of lime in 1971 was about \$15/ton, so this new potential represents a half-billion dollar market if the price level remains constant. If we reflect on what has happened to energy-related materials in the recent past, this price level will undoubtedly rise substantially if such a demand actually materializes.

CONCLUSIONS

(1) Both lime and limestone are reactants of interest to the utility industry for throwaway-scrubbing processes.

(2) If processes using limestone can be demonstrated to be reliable, the lower costs involved would obviously favor the use of limestone.

(3) No serious imbalances on a regional basis are foreseen at present for the limestone supply-demand relationship necessitated by the use of scrubbers. However, the purity of limestone which may be needed for successful operation could upset this balance.

(4) If lime is ultimately found to be essential, the overall impact of throwaway-scrubbing processes on the industry could be very serious in terms of current production and price levels.

(5) The major problem which remains is sludge disposal; this strongly encourages the utilities to look to alternate techniques which do not involve the use of throwaway-scrubbing systems and which do not employ either limestone or lime.

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FROM LIMESTONE TO LIME: A NEW CONCEPT IN GAS SCRUBBING

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ABSTRACT

The role of calcareous minerals in that area of the environmental improvement program involving the control or elimination of sulfur oxide emissions is discussed, and a new concept in gas scrubbing, rendering possible the use of calcareous rocks more extensively for this purpose, is presented. Calcareous rocks are defined as the more common limestones, consisting essentially of calcium carbonate and magnesium carbonate. The effect of magnesium carbonate on the reaction rate of limestones and lime toward sulfur oxides in aqueous scrubbing systems is pointed out. The relative economics of limestone versus lime as aqueous scrubbing reagents for sulfur dioxide are indicated.

The following remarks pertain to the role of calcareous minerals in that area of the environmental improvement program which involves the control or elimination of sulfur oxide emissions. For purposes of simplicity, "calcareous rocks" are defined as the more common limestones, consisting of calcium carbonate and magnesium carbonate.

Sulfur oxide emissions are considered to originate from coal-burning power plants and metallurgical smelters and to be essentially sulfur dioxide. When aqueous scrubbing of emissions is involved, sulfur dioxide produces an acidic solution which must usually be neutralized. Limestone, or the lime produced therefrom, can be used for this purpose as a reagent in an aqueous scrubbing system. Our remarks will touch briefly on technological and economic factors, comparing the merits of limestone and lime as scrubbing reagents, and then proceed to describe what is believed to be a novel scrubber for contacting sulfur acids with the neutralizing reagent.

As neutralizing reagents, limestones may be classified as high-calcium limestones, high-magnesium limestones, and dolomitic limestones. Almost all limestones of commerce

contain impurities to varying degrees; examples are silica and silicates, heavy metals, sulfides, and organic matter. However, for acid neutralization purposes, the presence of magnesium carbonate in the limestone is generally considered to be the major ingredient affecting the behavior of the limestone toward acids. The presence of magnesium carbonate in many limestones causes the reaction rate of the limestone to drop so sharply that limestones containing more than 5 percent magnesium carbonate may exhibit an impractical rate of reaction. Indeed, dolomitic limestone, being an equal molar mixture of calcium carbonate and magnesium carbonate, may be completely unsuited for sulfur oxide emission control in aqueous scrubbing systems (Hoak and others, 1945).

This paper will limit the technological and economic evaluation of limestone for gas scrubbing to high-calcium limestone containing less than 5 percent magnesium carbonate because this is the type of limestone which has, and is, finding application in sulfur oxide emission control (Slack and others, 1971). However, this is not to imply that the high-magnesium limestones ranging to the dolomites will not find similar applications, particularly when converted by cal-

cination to their corresponding quicklimes.

With reference to lime, the calcining operation apparently destroys the reaction rate effect of the magnesium. High-magnesium lime or dolomitic lime may have superior neutralizing characteristics. In the case of limes, therefore, the usual impurities, to which reference has already been made, become of great significance in determining the neutralizing value of the lime. It is beyond the scope of this presentation to discuss such relationships in great detail.

From a technological point of view, the major disadvantage of high-calcium limestone as a neutralizing reagent is that the limestone should, in order to react efficiently, be pulverized to at least a size that will pass a 200-mesh standard sieve. Unfortunately, the smaller particles of the pulverized limestone react first when the system is at its point of greatest acid strength, thereby forcing the ever-increasing coarse remainder of the limestone to react under conditions of least driving force. For this reason, the stoichiometry of the limestone reaction in aqueous scrubbers is generally much less than desired. This may require a range of from 25 percent excess limestone in the scrubber to as much as 200 percent excess in order that the neutralizing reaction may be carried out in a time period compatible with the retention characteristics of the scrubber. At the present time, an average stoichiometry for limestone usage in wet scrubbers is considered to be about 1.5 times theoretical.

Although this relatively poor stoichiometry obviously has an economic impact on limestone usage, the major economic disadvantage of limestone in aqueous scrubbing systems is the useless burden of carbon dioxide which accompanies limestone from the ground to its point of application in the scrubber. Ignoring the normal impurities, high-calcium limestone is approximately 56 percent calcium oxide equivalent. In other words, for every 100 tons of limestone removed from the ground, crushed, pulverized, transported to point of use, stored, and rehandled, only 56 tons are finally available, assuming perfect stoichiometry. This consideration weighs heavily in the choice between limestone and lime and eliminates limestone from consideration unless the limestone source is at or very near the point of application in the gas scrubber.

On the other hand, the lime which can be produced from the limestone by calcination exhibits excellent stoichiometry in gas-scrubbing operations and is in a much more favorable economic situation from the standpoint of transportation and application because the unwanted bur-

den of carbon dioxide has been driven off during the calcining operation. Studies have been undertaken and reported on the relative neutralizing value of limestones and limes; such relative values are referred to as "basicity factors" (Hoak and others, 1944). The basicity factor compensates for impurities which are nonreactive in acids, but does not compensate for stoichiometry where retention time to effect a complete reaction is critical. In essence the basicity factor is determined by boiling a weighed quantity of the limestone or lime in a measured volume of a standard acid for a specific time period and then back-titrating the remaining acid to determine the true neutralizing value (basicity factor) of the limestone or lime. Based on this relationship, as referred to a unit of pure calcium oxide, the relative neutralizing value of any material of interest can be used in economic appraisals. Table 1 illustrates some basicity factors that may be obtained by experiment.

Using stoichiometric considerations and basicity factors, it is possible to calculate the cost of a unit of neutralizing value in a sulfur oxide scrubber. The exercise in calculation presented in table 2 is for illustrative purposes only. Although the price figures used are believed to be reasonably realistic at present, the figures are fictitious and do not represent an actual situation. It can be noted that the simple formula used for calculating unit cost of neutralizing reagent is: (1) cost at point of application divided by (2) basicity factor multiplied by (3) stoichiometry. Only the major cost items are indicated.

The size-reduction cost for quicklime is relatively low because this is a simple lime-slaking operation in which the quicklime automatically disintegrates to essentially minus 200 mesh in the presence of water. Also, it should be mentioned that the size-reduction cost for pulverizing the limestone does not include cost and operation of dust-control equipment, which would likely be necessary.

Now, as the foregoing considerations relate to the actual gas-scrubbing operation using limestone or lime, both materials will generally be found to be the least expensive reagents in cases where aqueous gas scrubbing can be undertaken in the first place. There are many situations in which aqueous scrubbing cannot be applied because of problems arising from the disposal of the huge volumes of wet calcium sulfite sludge created by the scrubbing operation (Lewis, 1972). Also, there are circumstances wherein high-magnesium limes may cause water-pollution problems because of the solubility of some magnesium salts. Evaluations of this nature are beyond the scope of this paper.

TABLE 1. - Comparison of chemical equivalents of liming materials

Liming material	Descriptive formula	Approximate basicity factor*
Dolomitic quicklime	$\text{CaO} \cdot \text{MgO}$	1.12
High-calcium quicklime	CaO	0.96
Normal dolomitic hydrate	$\text{Ca}(\text{OH})_2 \cdot \text{MgO}$	0.88
Dolomitic pressure hydrate	$\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2$	0.83
High-calcium hydrate	$\text{Ca}(\text{OH})_2$	0.71
Dolomitic pulverized limestone	$\text{CaCO}_3 \cdot \text{MgCO}_3$	0.58
High-calcium pulverized limestone	CaCO_3	0.54

*Basicity factor = gram equivalent CaO per gram of liming material.

When scrubbing is otherwise feasible, the problem has been, and at present continues to be, that the various types of scrubbers available tend to plug with chemical precipitate and extraneous particulate matter, such as fly ash, to a point where the scrubber becomes inoperable. Too frequent shutdowns for cleanout then render the gas-scrubbing system impractical. If air pollution abatement standards are to be met and maintained it is imperative that the gas-scrubbing systems involved yield long and trouble-free operation.

The National Lime Association has undertaken the development of an aqueous scrubber which can operate indefinitely without plugging by chemical precipitates or extraneous particulate matter. A pilot version of this scrubber

has been under test for almost three years with practically trouble-free operation. It is believed that the design of this scrubber assures the removal of sulfur dioxide gases by wet scrubbing, using whatever scrubbing reagent is the most economical, but especially limestone and lime, which, as has already been stated, are the lowest priced abundant reagents available for this purpose. It is significant that test work to date on the Lewis scrubber has indicated the scrubber operates efficiently on lime slurry, thus rendering possible the use of what may be the most economic reagent in most locales.

The Lewis scrubber is a horizontal rotating tube patterned after a rotary lime kiln. In the interior of the rotating cylinder are chain suspensions, which gently police the inside walls of

TABLE 2. - Sample comparison of costs for three scrubbing reagents

	High-calcium limestone	High-calcium quicklime	Dolomitic quicklime
F. o. b. source	\$ 3.00	\$21.00	\$22.00
Freight	4.50	4.50	4.50
Size reduction	4.00	0.25	0.25
Total A	\$11.50	\$25.75	\$26.75
Equivalent calcium oxide (B. F. *)	0.54	0.96	1.12
A ÷ B. F. Total B	\$21.30	\$26.82	\$23.88
Stoichiometry (average) Total C	1.50	1.10	1.10
Final cost of unit CaO (total B x total C)	\$31.95	\$29.50	\$26.27

*Equivalent calcium oxide from Lewis and Yost (1950).

the cylinder and also continuously flex as the cylinder rotates, allowing the collapsing chains to dip into the pool of aqueous lime slurry in the bottom of the cylinder and to carry the slurry as the cylinder rotates. This concept permits absolute control of the retention of the aqueous scrubbing medium in the cylinder because rate of discharge is completely dependent on the rate at which the aqueous scrubbing medium is pumped into the cylinder. Such retention time allows excellent control of the pH of the sludge discharge, thus rendering recycle in this scrubbing system unnecessary. Pressure drops are gratifyingly low because the gases are not passed through liquids, but only through very tortuous pathways, which allow impingement of the gases on the always fresh surfaces of the scrubbing medium adhering to the chains. Other advantages of this system appear in the cited references.

To date, the original pilot model of the Lewis scrubber has operated with good results on the off gases of a coal-burning power plant using low-sulfur western coal, on similar gases from coal-burning utilities using high-sulfur eastern coal, and on the stack gases of a smelter processing a metal sulfide concentrate. All of these operations were downstream from electrostatic precipitators so that, although the scrubber was doing an excellent job on sulfur dioxide removal, it could not be ascertained whether or not the scrubber would simultaneously remove fly ash without benefit of electrostatic precipitators ahead of the scrubber. Recently, however, a larger pilot version of the scrubber has been operating on the off gases from a coal-fired boiler of a sugar

mill. This operation is without benefit of a settling chamber or electrostatic precipitator ahead of the scrubber which accepts the raw boiler gases, including the total burden of fly ash. As expected, sulfur dioxide removal was up to expectation, but the scrubber was also highly effective in removing the fly ash particulates. At a loading of approximately 0.4 grain of particulates per actual cubic foot in the input gas, the exit gases from the scrubber contained approximately 0.03 grain per actual cubic foot. It is believed that with minor modifications of the scrubber the removal of particulates can be further improved.

As for the economics of this scrubber, pilot experience to date indicates a favorable situation. The major disadvantage is that mechanical considerations limit the cross-sectional area of the Lewis scrubber to diameters comparable to those possible for rotary cement kilns; however, the overriding advantage of the scrubber is that it cannot plug with scale and particulates. Furthermore, the incorporation of this scrubber into a total air-cleaning system should eliminate much costly ancillary equipment such as electrostatic precipitators, lime slakers, recycle equipment, and thickeners. This circumstance should reduce the capital investment for the total gas-scrubbing system. Also, it is postulated that additional savings should be realized by virtue of the lower operating costs related to decreased maintenance, draft-fan horsepower reduction, and improved stoichiometry. It is believed the foregoing economic appraisal is reasonable, although a conclusive analysis on this must await additional operating data.

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DISPOSAL OF BY-PRODUCTS FROM LIME AND LIMESTONE SCRUBBERS AT COAL-BURNING PLANTS

by

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ABSTRACT

Current developments in using lime and limestone slurries to remove sulfur oxide gases from the stacks of coal- and oil-burning furnaces have established an important need for treatment systems which include adequate disposal of resulting waste materials. The paper briefly outlines the classes of scrubbers which are using lime and limestone and describes the characteristics of the by-product material being produced. Some discussion is also included relating to methods of disposal of the scrubber underflow. Since coal-burning plants also produce fly ash as a waste material, one system developed by the author's company combines this material with the sulfur oxide by-products. The mixture is processed in a manner which converts the waste products into usable materials with acceptable structural and environmental properties. Recent interest in protection of ground waters from heavy-metal leachates has made the fly ash-sulfur oxide system an acceptable means of disposal, because the conversion products have very low permeability and adequately encapsulate soluble salts within the hardened mass.

Although only limited information is available on the types and chemical requirements of limestone used in these processes, a few guidelines are presented to indicate the range of materials that can be used with good results.

INTRODUCTION

The importance of using coal as a primary energy source in America has received considerable attention in recent months. Fortunately, various technologies are being developed which will enable combustion processes to burn this fuel and, at the same time, provide clean stack gases which will have little deleterious effect on the environment. The extensive effort which has gone into the development of lime and limestone scrubbers to achieve the latter objective has resulted in the development of several commercial systems which should become reliable in the near future. Evaluation of these systems by a number of organizations, such as the U. S. Environmental Protection Agency and the U. S. Bureau of Mines, indicates that by 1980 it is quite possi-

ble that very large quantities of by-product materials can be expected to be generated from coal-burning operations. Table 1 gives a few projections supplied by one of these organizations (Evans, 1973).

Several papers being presented in this seminar relate to the operation of scrubbers which use lime or limestone to absorb the sulfur oxides in the stack gases. Although there are a number of scrubber manufacturers that promote these types of systems, in essence they can be divided into three general categories: limestone, hydrated lime, and double-alkali systems. Scrubbers are currently being evaluated with each of these systems in both pilot and full-scale operations.

The double-alkali system might be further divided to include the various processes in which the lime or limestone addition is made outside the

TABLE 1. - Estimates of solid-waste production from the lime desulfurization process

	Example 1, 000 Mw	1975 7, 000 Mw*	1980 86, 000 Mw**
Production rate (millions of tons, 50 percent solids)	0. 83	5. 81	71. 38
Disposal area (acres, 20-yr. lifetime, 20-ft. depth)	43	301	3, 698

*Estimate is based on existing and planned lime- or limestone-scrubbing facilities.

**Estimate is based on projected coal consumption by electric utilities in 1980.

scrubber itself. In one instance this simply means that the scrubber operates at a low pH to prevent supersaturation of calcium sulfate and other calcium compounds that can cause plugging of the scrubber. After the slurry leaves the scrubber, lime is added to precipitate the calcium sulfite (and sulfate). Most of this treated slurry is then returned to the scrubber to act as the absorbent (in this case resulting in the formation of calcium bisulfite). Other systems employ a different alkali, such as sodium carbonate or ammonia, in the scrubber. As in the previous example, the scrubber effluent is treated with lime or limestone to precipitate the previously formed sulfur oxide compounds as calcium sulfites or sulfates. Scrubbers are also used as a means of removing residual fly ash from the stack emission. This by-product may therefore be present in varying proportions in many of the effluents of the scrubber systems.

The major by-product that is generated in all of these processes is a combination of calcium sulfite and sulfate. In addition, the discharge contains large quantities of water. From the standpoint of disposal the removal, handling, and disposition of this water plays an important part in the control of the scrubber discharge. Other by-products, such as salts of sodium, ammonium, magnesium, etc., may also be present (generally to a minor degree).

In a few instances the scrubber system is designed to oxidize the discharged sulfite completely to sulfate to assist in the dewatering of the slurry. Some efforts have also been undertaken to prevent oxidation in order to avoid in the recycle of slurry a deposition of scale within the scrubber or demister vessel.

In the case where scrubbers are applied to oil-burning furnaces, the same constituents are found in the slurry, with the exception that very little, if any, fly ash is produced.

In developing a technology to handle the underflow from the scrubber systems, it is essential to recognize that the waste material must be concentrated to a point where it can be disposed of beneficially. Since most of the scrubber underflows contain a solids content of approximately 5 percent (by weight), many plants use a primary thickener to bring the solids concentration up into a range of 30-40 percent. An exception to this last statement might be the unique scrubber developed by Cliff Lewis, who is participating in this seminar. It has been claimed that this particular scrubber can discharge a much higher solids content in the effluent, thereby simplifying the dewatering procedures.

IU Conversion Systems has had an opportunity to investigate a large number of samples of underflow from SO₂-scrubbing systems. Most of the material was derived from limestone scrubbers, although more recently the by-product sludges from lime and double-alkali scrubbing systems have become available. Unfortunately, many of the scrubbers had operational difficulties, and the samples were not always representative (based on the manufacturer's design criteria). This is particularly the case with limestone scrubbers because the yields of reaction products were commonly quite poor, resulting in a large surplus of unreacted calcium carbonate in the samples. Rather than discuss these complicating effects, it is felt that for the purpose of this presentation examples should be selected of scrubber discharge representative of the type of product that is obtained

TABLE 2. -Selected analyses of calcitic lime-limestone sludges

No.	Scrubber type	Scrubbing medium	Basis of analysis	Weight of dry solids (%)					
				$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaCO_3	Inerts	Fly ash	Ca(OH)_2
1	Turbulent contact	Limestone	Total effluent	25	25	25	--	25	--
			Non-fly ash basis	33	33	33	--	--	--
2	Turbulent contact	Limestone	Total effluent	45	38	14	2.5	0.2	--
3	Marble bed	Limestone	Total effluent	30	40	19	4.5	6.5	--
4	Marble bed	Lime	Total effluent	50	44	--	1.4	0.2	4
5	Venturi	Lime	Total effluent	41	9	17.5	3.5	22.5	6.5
			Non-fly ash basis	53	11	23	4	--	8
6	Venturi	Lime	Total effluent	39	4	5	--	40	12
			Non-fly ash basis	63	7	8	--	--	20
7	Horizontal spray tower	Lime	Total effluent	37	50	--	3	7.5	2.2

when the scrubbing system is performing properly. Table 2 lists the compositions of several typical scrubber-discharge sludges under conditions stated to be optimum. The analyses are exclusive of magnesium compounds (MgSO_3 / MgSO_4 and MgCO_3) because these were found to be quite variable and generally in low concentration. On the other hand, sludge from a Venturi scrubber using monohydrated lime produces, in addition to $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, large quantities of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ (up to 25 percent by weight of dry solids) and small quantities of Mg(OH)_2 . Samples of sludge from a double-alkali system contained very high concentrations of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, indicating that in this instance calcium sulfite was oxidized prior to dewatering of the sludge. Sodium salts were also present in amounts ranging from approximately 1 to 5 percent by weight of dry solids.

DISPOSAL SYSTEMS

One of the commonly used methods which has been considered for disposal of by-product sludges consists of simply transporting the material to a waste pond or lagoon. Unfortunately this practice is rapidly becoming quite undesirable because of the various problems created by a throwaway-lagoon system. Among the problems are the difficulty in finding suitable disposal sites, the rising costs of removal to the sites, the effect of leachates from the ponds on the environment, and the fact that the disposal site becomes virtually unavailable for future

use, thus resulting in large wasteland areas. Samples removed from sludges that have similar rheological properties and that have been ponded for fifty years are found to be still in a wet soft unusable condition. The objective then is to find ways of converting this material into a more acceptable form so that if it is to be used as a landfill it will have the proper structural characteristics and environmental properties. This inevitably leads to some type of chemical treatment, either the use of admixtures or the use of other specialized techniques.

The particular method that has been developed by IU Conversion Systems is an example of one procedure which has been found to be eminently suitable for the disposal of these by-product materials. The process is basically an outgrowth of previous programs related to the utilization of fly ash from pulverized-coal-burning operations. The technology therefore not only affords a means of disposal of sludge, but also establishes a useful method of disposition of by-product fly ash. Fortunately, the amount of available fly ash produced in the power plants is sufficient to prepare a variety of compositions that upon aging, or curing, undergo complex chemical changes which can stabilize the final product. The chemistry depends in part upon the interaction of some of the constituents in the fly ash (glassy Al_2O_3 and SiO_2) and the calcium (and magnesium) sulfites and sulfates. With proper inclusion of additive materials as may be required and with proper proportioning and handling of the materials involved, stable cementitious compounds are produced and cause the sludge-fly-ash mixture to harden into

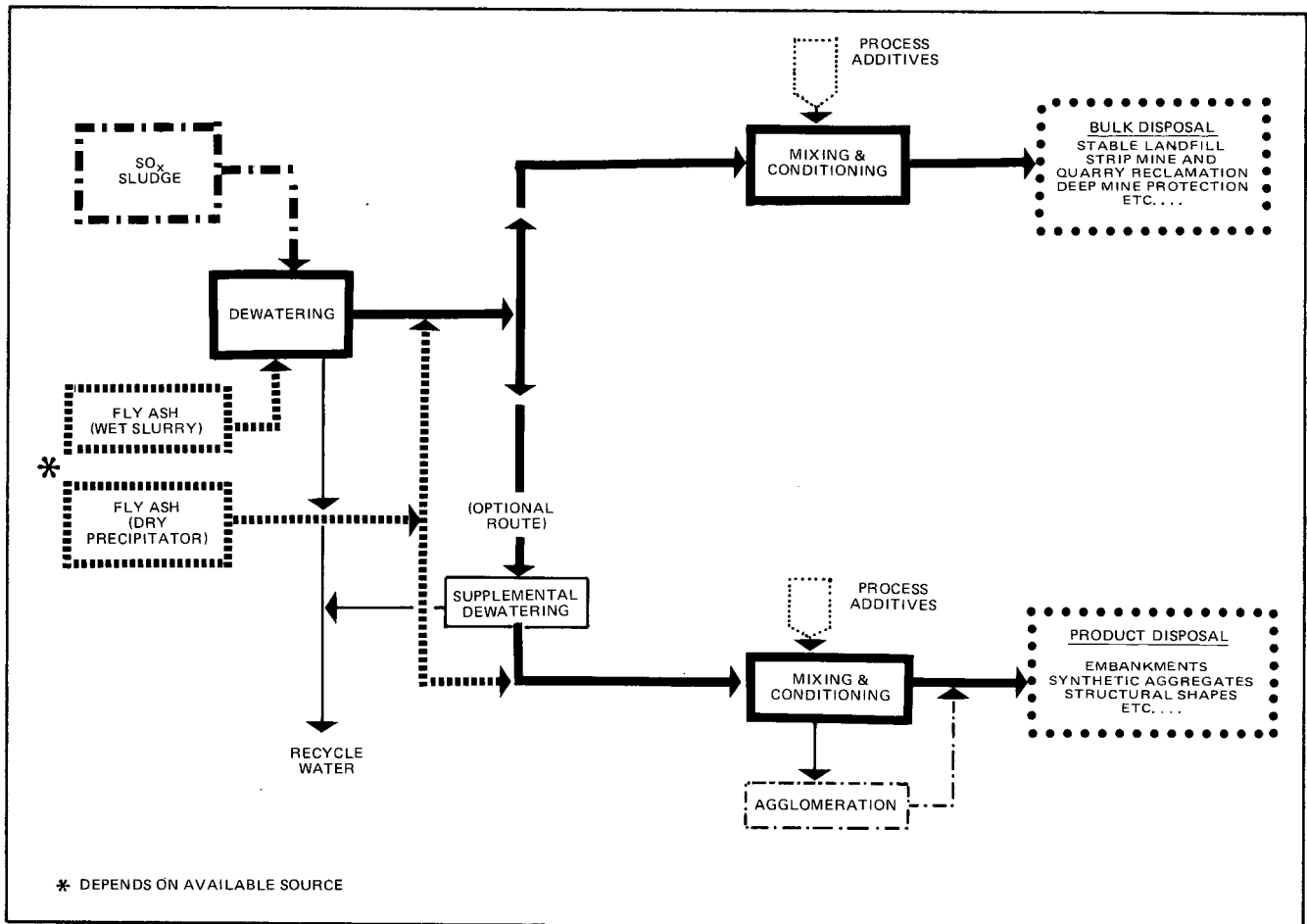


FIGURE 1. - Schematic diagram of IU Conversion Systems, Inc., waste conversion process.

strong durable compositions with low permeability.

Figure 1 is a schematic diagram of the IUCS sludge treatment process as it applies to lime- and limestone-scrubber sludges. As shown in the figure, the conversion process first combines fly ash and small quantities of proprietary additives with the scrubber sludge. The fly ash can be supplied either in wet condition as a slurry, or directly from electrostatic precipitators in dry form. Depending on the degree of dewatering and conditioning, a variety of usable products can then be produced; these range from stabilized landfill to compositions with structural properties suitable for use in the construction of dams and reservoirs and in synthetic aggregates. Among the properties that relate to applications of these conversion products are those dealing with strength, durability, dimensional stability, and permeability of the final mixture.

Figures 2 and 3 present graphically examples of penetration resistance and compressive

strength that can be developed in applications such as a structural landfill.

Figure 4 shows the influence of additive concentration in developing dimensional properties. It will be noted that there is a slight expansion at early ages (during the hardening of the mass), after which no more volume change occurs. This nominal expansion has the advantage of preventing cracking in large sections.

Figure 5 presents a relatively high strength nonplastic sludge-fly-ash mixture and a conventional fly-ash composition.

Figure 6 shows comparisons made between a typical fly-ash stabilized base and a sludge-fly-ash mixture as relating to the permeability. The very low permeability of the sludge formulation serves as a protection against leaching of ions into the subgrade.

A number of previous publications (Minnick, 1973a, b; 1974) have described other details of the system; these details are therefore not included in this presentation.

LIME AND LIMESTONE PROPERTIES RELATING TO SO₂-SCRUBBER APPLICATIONS

It is understood that several papers at this meeting consider the types of limestone that are contemplated for use in SO₂-scrubber applications. At the present time there is limited information available in the literature dealing with this subject, although considerable work has been undertaken by various organizations (including the company with which this writer has been associated). A few appropriate comments can be made with respect to these investigations.

In one study (Saleem, 1972) the evidence shows clearly that when limestone is used for the scrubbing operation calcitic materials perform much better than dolomites. Calcitic limestones also show considerable differences in ability to react with the sulfur oxide. In addition to the purity of the stone, physical properties substantially influence the reactivity. These properties include specifically hardness, density, and porosity. A report (Drehmel, 1972) dealing with dissolution rates of limestone has indicated that the best types of carbonate rock tested for batch-scrubbing efficiency were marl and chalk. Other important considerations in limestone scrubbers are the pH of the system and to some degree the fineness to which the limestone rock is ground.

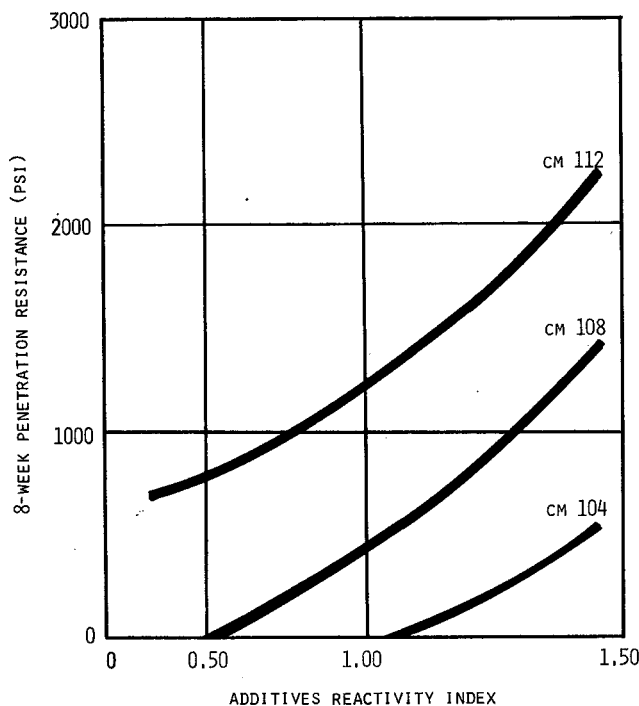


FIGURE 2. - Modified Vicat penetration resistance for several sludge-fly-ash compositions.

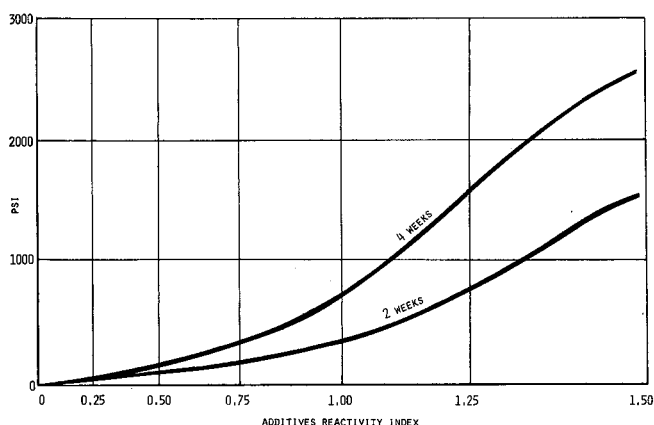


FIGURE 3. - Unconfined compressive strengths (2-inch cubes) for sludge-fly-ash mixtures for landfill-type applications.

In contacting a number of plants where limestone is being used for SO₂ scrubbing, it was learned that the size most commonly being employed is minus 200 mesh.

As mentioned previously, many of the scrubber sludges which have been tested in the author's laboratory have indicated that very large percentages of the carbonate rock are found to be in unreacted condition in the samples. It has been stated, however, that when these scrubbers operate properly it is only necessary to employ in the neighborhood of 20 percent excess over the stoichiometric requirement of the scrubber system.

In the case where lime scrubbing is employed, it has been noted that generally the reaction proceeds at a much more favorable rate. It is evident also that the presence of magnesium oxide not only does not interfere with this reaction but, in fact, when properly utilized can show some advantages over the high-calcium materials. One

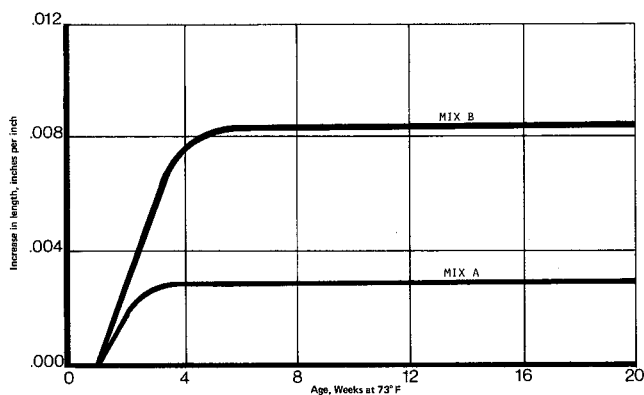


FIGURE 4. - Early expansion of sludge-fly-ash mixtures.

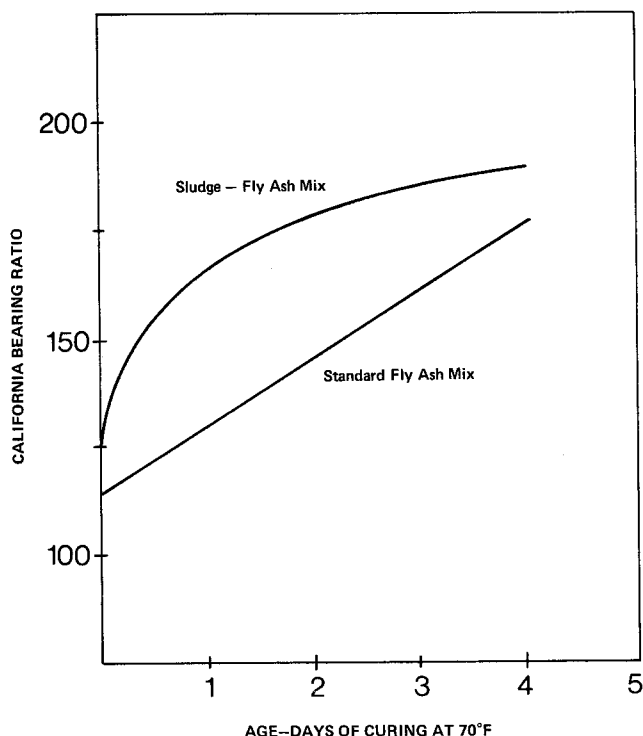


FIGURE 5. - Comparison of California bearing ratios for IU Conversion Systems, Inc., sludge-fly-ash product and conventional fly-ash composition.

scrubber which has been reported earlier in the literature (Bitler and Minnick, 1973) has been on stream for several years and is performing extremely well using a monohydrated dolomitic lime.

In order to establish specifications for lime or limestone for use with scrubber systems, the procedure to date has been primarily to request suppliers to provide materials that meet existing ASTM specifications. These specifications are for commercial grades of lime and limestone of relatively high purity, grades normally used by the chemical industry or for trade-waste purposes. On the other hand, it has been demonstrated that some low-quality limes can perform equally well. By-product calcium hydroxides are also being used in full-scale scrubbing operations quite successfully (Sakanishi and Quig, 1973; Louisville Gas and Electric Company, 1974). Certain selected specifications are currently being developed by scrubber manufacturers after extensive tests in their pilot plant operations. These latter specifications normally include maximum limits for silicon dioxide and iron and aluminum oxides, as well as a requirement (such as an ASTM slaking test) for lime

reactivity.

With respect to the availability of limestones for the projected needs of the power industry, one report (O'Donnell and Sliger, 1971) has indicated that enormous deposits of carbonate rocks exist in the United States and that these reserves are more than adequate for the foreseeable future. The report points out also that the larger deposits of carbonate rock are found generally in those areas where fossil-fuel-fired power plants are located.

Although the O'Donnell and Sliger report would appear to be favorable for providing adequate supplies of lime or limestone to the scrubber, it should be recognized that numerous difficulties may be encountered in opening new quarry sites. Land acquisition, zoning, conservation limitations, and numerous other political considerations may prevent extraction in some areas. On the other hand, quarries may be reclaimed by recycling the stabilized disposal product from the conversion system either as a landfill or as a storage site for aggregate or other by-products.

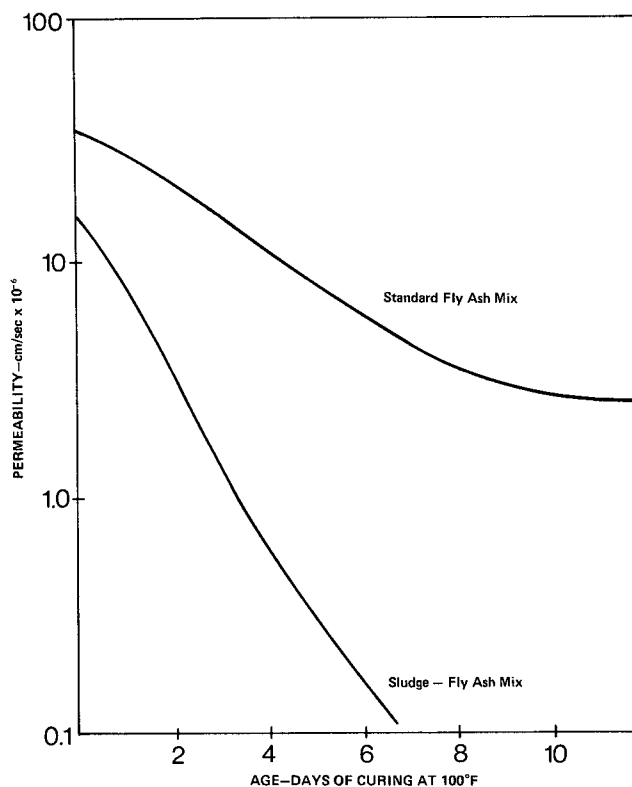


FIGURE 6. - Comparison of permeability values for IU Conversion Systems, Inc., sludge-fly-ash product and conventional fly-ash composition.

SUMMARY

Based on the present state of the art, it can be concluded that cleaning of stack gases by means of scrubbing systems which use lime or limestone does offer a viable solution to controlling air pollution from coal-burning operations. It is indicated that lime may offer the best type of alkali, either alone or in conjunction with other alkalies, for use in the scrubber systems, although limestone also is being evaluated in a number of instances. Owing to difficulties in

opening new quarrying operations, availability of acceptable limestone represents a problem, although ample sources of supply have been identified in most coal-burning areas. Available technology to dispose of the by-product sludge from the scrubber can also provide useful products for land rehabilitation, synthetic aggregates, and various other applications that meet structural and environmental requirements. The by-product disposal makes use of the fly ash, which is generally collected separately, either in electrostatic precipitators or in a separate scrubber system.

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